THE REACTIONS OF IODINE ATOMS IN THE GAS PHASE

by

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DISCUSSION

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ABSTRACT

The gas phase reactions of iodine atoms with ethane, propane, isobutane and normal butane have been studied in a high vacuum system of conventional design. The apparatus was constructed of pyrex glass and the section used for handling iodine was fitted with greaseless metal valves and maintained at 120°C in a heated box. Product analysis was by gas liquid and gas solid chromatography.

The mechanism assumed for the reactions mentioned above is described by reactions one to six written below.

$$I_2 + M \longrightarrow 2I + M \qquad 1$$

$$I + RH \longrightarrow HI + R \qquad 2$$

$$R + I_2 \longrightarrow RI + I \qquad 3$$

$$R + HI \longrightarrow RH + I \qquad 4$$

$$I + RI \longrightarrow R + I_2 \qquad 5$$

$$I + I + M \longrightarrow I_2 + M \qquad 6$$

Absolute values for k_2, the rate constant of reaction 2, have been measured for ethane, propane and isobutane and the Arrhenius parameters for these reactions calculated. The activation energies combined with accurate estimates for that of reaction 4 have been used to calculate the endothermicity of reaction 2 and these reaction heats combined with knowledge of the bond dissociation energy of HI have led to values for the C-H bond dissociation energies in ethane, the secondary position in propane and the tertiary position in isobutane. The data for the Arrhenius parameters of reaction 2 and the C-H bond dissociation energies are tabulated below. Other related thermochemical data has been calculated from these bond strength values.

Data/

Data for Reaction 2

Hydrocarbon	E_{act} kcal.mole^{-1}	logA_{-1} (c.c.mole.$^{-1}$ sec.$^{-1}$)	D (R-H) (25°C) kcal.mole^{-1}
C_2H_6	26.3 ± 0.9	14.23 ± 0.4	96.4
C_3H_8	24.6 ± 1.0	14.26 ± 0.4	94.2 (sec.H)
iC_4H_{10}	21.6 ± 0.8	13.88 ± 0.31	91.1 (tert.H)

The probable errors (0.676) are quoted.

Consideration of the fall off in the rate of product formation with time in the above reactions has enabled estimates to be made of the rate constant ratio k_4/k_3.

Rate constants have not been determined for the reaction of iodine with n-butane but the reaction products have been characterised and the importance of secondary product formation at 300°C has been demonstrated.

Aromatic products have been detected in reactions which were allowed to proceed for several hours at 300°C and a mechanism for their formation based on the abstraction of hydrogen atoms by iodine atoms has been suggested.

CHAPTER I

GENERAL INTRODUCTION

The reactions of the halogens with hydrogen and hydrocarbons in the gas phase have proved to be important sources of information in the understanding of the mechanism of many gas phase reactions and in the evaluation of the theories of chemical kinetics. The classical studies were carried out by Bodenstein[1,2] and his co-workers, who derived overall rate expressions for the reactions of iodine and bromine with hydrogen. The expression for the iodine reaction was of a simple second order type and it was deduced that the reaction proceeded by a bimolecular mechanism. The expression obtained for the bromine reaction was of a complex type and it was 1919 before Christiansen[3], Hertzfeld[4] and Polanyi[5] were able to explain it by introducing the idea that free atoms could participate as independent species in chemical reactions. Nernst[6,7] about this time gave a similar explanation to account for the results of the reaction of chlorine with hydrogen. The introduction of the concept that gas phase reactions could consist of a series of elementary reactions caused a switch in the emphasis of chemical kinetic research from the measurement of overall reaction rates to the determination of the mechanism of reactions and the measurement of the rates of the elementary steps which combine to produce the overall reaction. The understanding of the complex nature of many gas reactions allowed the theoretical side of the subject to proceed. It is in the provision of experimental rate data for elementary reactions that the gas phase reactions of the halogens have proved to be of value.

I.1 THEORY OF REACTION RATES

This section is not intended as a rigorous account of the theories of chemical kinetics but its aim is to indicate the major concepts of the subject and the theoretical solutions to the problem of the calculation of the rates of chemical reaction.

1.1 The Arrhenius Equation

Towards the end of the 19th century van't Hoff suggested that the logarithm of the rate constant of a reaction should bear a linear relationship to the reciprocal of the absolute temperature. Arrhenius [8] was able to show that this was true for a number of reactions and that the equation had the form:

$$\ln k = \ln A - E/RT$$

where the symbol R stands for the gas constant, T is the absolute temperature and A and E are known as the 'A' factor and activation energy of the reaction respectively. The values of A and E are characteristic for each chemical reaction. Arrhenius introduced the idea that reaction proceeded via active molecules which were in equilibrium with the normal species. The Maxwell-Boltzmann Distribution Law gives the fraction of molecules in a gas having energy greater than E in two degrees of freedom as;

$$\frac{n_e}{n_o} = e^{-E/RT}$$

and comparison of this equation with the Arrhenius equation written in the form;

$$k = A\, e^{-E/RT}$$

suggests that the difference between the active and normal molecules is their energy and only those with energy in excess of a minimum amount, E, are capable of reacting. If one is to calculate the rates of chemical reaction one must be able to calculate values for A and E.

1.2 The Activated Complex

When two reacting species come together they are considered to form an activated complex which in turn decomposes to give the reaction products. Consider a potential energy diagram for a system of three atoms (fig. 1), which can react in the following manner,

$$X + YZ = XY + Z.$$

The potential energy of the system is plotted against the reaction co-ordinate which represents the conversion of reactants to products. The potential energy increases to a maximum at the point where the three atoms form the activated complex. The activation energy can be seen to be the energy difference between the reactants and the activated complex and the heat of reaction is the energy difference between reactants and products.

1.3 Calculation of Activation Energies

London [9] introduced the view that the theoretical calculation of the activation energy of a reaction, such as represented in figure 1, would require the construction of the complete range of potential energy surfaces for the three atom system and hence determination of the path of lowest energy for the conversion of reactants to products. This would involve the calculation of the potential energy of the system treating the distances X-Y (R_{x-y}), Y-Z (R_{y-z}) and X-Z (R_{x-z}) as variables. A simplifying feature indicated by London was that most chemical reactions are electronically adiabatic and this means that the reaction proceeds on one potential energy surface.

The potential energy of a system of three atoms is given by [10];

$$E = X + Y + Z + \left(\tfrac{1}{2}\left[(x-y)^2 + (x-z)^2 + (y-z)^2\right]\right)^{\frac{1}{2}}$$

where X + x, Y + y and Z + z are the energies of the three possible pairs XY, YZ and XZ. The potential energy related to the interaction of the atoms is divided into two parts viz. the coulombic or electrostatic energies X, Y and Z and the exchange or resonance energies x, y and z. The sum of the/

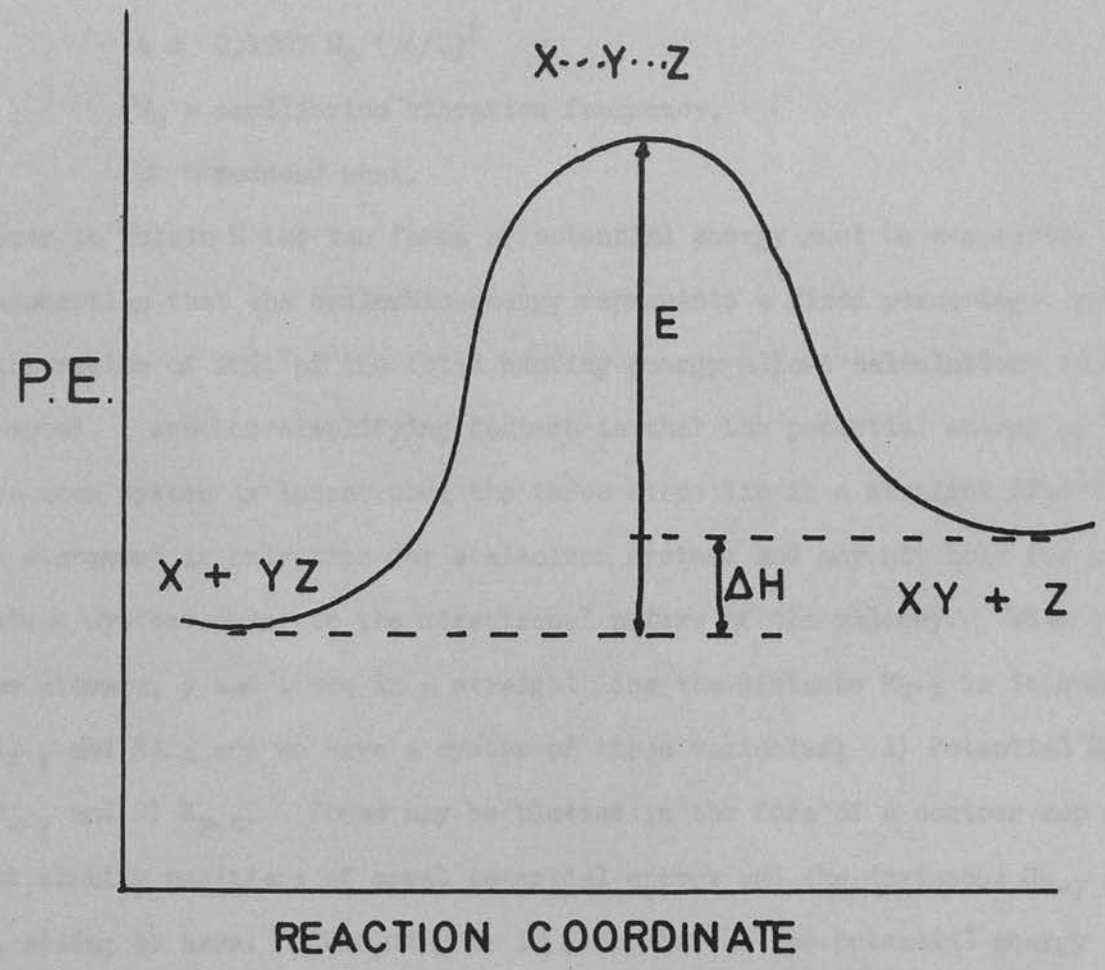


FIGURE-1 POTENTIAL ENERGY DIAGRAM FOR THE REACTION

$$X + YZ \longrightarrow XY + Z$$

/the two energies can be obtained from spectroscopic data using the Morse equation:

$$E' = D' \left(e^{-2a(r-r_o)} - 2e^{-a(r-r_o)}\right)$$

where D' = heat of dissociation of the molecule + zero point energy

r_o = equilibrium interatomic distance of the normal molecule.

$$a = 0.1227\, W_o\, (\mu/D)^{\frac{1}{2}}$$

W_o = equilibrium vibration frequency.

μ = reduced mass.

However to obtain E the two forms of potential energy must be separable. An assumption that the coulombic energy represents a fixed percentage, generally in the region of 20%, of the total binding energy allows calculations to be attempted. Another simplifying feature is that the potential energy of the three atom system is lowest when the three atoms lie in a straight line[11]. This statement is only true for s electron systems and may not hold for p electron systems owing to the directional nature of the valency. When the three atoms x, y and z are in a straight line the distance R_{x-z} is dependent on R_{x-y} and R_{y-z} and we have a system of three variables; 1) Potential Energy 2) R_{x-y} and 3) R_{y-z}. These may be plotted in the form of a contour map with lines linking positions of equal potential energy and the distances R_{x-y} and R_{y-z} acting as axes. This diagram is described as the potential energy surface for the reaction. It can be made to yield information regarding the distribution of vibrational and translational energy in the system by drawing the axes at an appropriate angle such that the interchange of potential and kinetic energy of a particle, moving under the influence of gravity and free from frictional effects, will represent the energy interchanges in the reacting system [12]. Once this diagram is constructed it is possible to trace the path of minimum energy for the reaction and obtain an estimate of the activation energy./

/energy. The construction of such a diagram is a process of some complexity and has only been attempted for a small number of systems. Eyring and Polanyi[13] applied the method to the reaction of a hydrogen atom with a hydrogen molecule.

$$H + H_2(p) \longrightarrow H_2(o) + H$$

This reaction has been studied between 0 and 100°C[13] and 600° to 900°C[14] and the experimental activation energy found to be 6 kcal. mole^{-1}. Taking the coulombic share of the potential energy to be 20% the activation energy was found to be 7.6 kcal. mole^{-1}. It is worth noting that if P.E. (Coulombic) is taken as 14% the calculation gives E (activation) as 14 kcal. mole^{-1} and this type of result along with consideration of the approximations in the derivation of the London equation make the results of these calculations more of qualitative than quantitative interest.

1.4 Collision Theory of Reaction Rates

McLewis[15] in 1923 applied the simple kinetic theory of gases to the problem of the estimation of the A factor. The basis of the theory was the idea that the Arrhenius equation represented the product of the proportion of molecules with enough energy to react and the total number of collisions in unit time. The kinetic theory of gases equation for the number of collisions (Z) in the gas phase between two species X and Y is:

$$Z = Nx\ Ny\ \sigma_{xy}^2 (8\pi kT/\mu)^{\frac{1}{2}} \text{ molecules cc}^{-1} \text{ sec.}^{-1}$$

where Nx and Ny represent the concentrations of X and Y in molecules cc^{-1}, σ_{xy} is the mean collision diameter of X and Y, μ is the reduced mass of the collisional complex, k is the Boltzmann constant and π and T have their conventional meaning. The reaction rate is given by:

$$\frac{d(\text{Products})}{dt} = k(X)(Y) = kNxNy = Ze^{-E/RT}$$

Therefore/

/Therefore $k = \frac{Z}{NxNy} e^{-E/RT} = \sigma xy^2(8\pi kT/\mu)^{\frac{1}{2}} e^{-E/RT}$

$= Z' e^{-E/RT}$

The symbol Z' is known as the standard collision number and is the number of collisions for a concentration of one molecule cc^{-1} $sec.^{-1}$. The A factors of a number of reactions do approximate to Z' but a large number do not. To explain the discrepancy between theory and experimental results a factor P was introduced such that:

$k = PZ' e^{-E/RT}$

The symbol P is called the steric factor as it was assumed that the error between theory and experimental was due to reactions having configurational requirements which the reacting molecules had to meet when in collision. The "steric requirement" theory could not explain the fact that occasionally the value of A found by experiment was greater than Z'. A theoretical weakness exists in the idea of a steric factor and this may be detected if we consider the equilibrium constant for the system:

$X_2 + Y_2 \rightleftharpoons 2XY$

The equilibrium constant may be written

$$K_{12} = \frac{k1}{k2} = \frac{P_1Z_1 e^{-E_1/RT}}{P_2Z_2 e^{-E_2/RT}}$$

$$= \frac{P_1Z_1}{P_2Z_2} e^{-(E_1-E_2)/RT} = \frac{P_1Z_1}{P_2Z_2} e^{-\Delta H/RT}$$

Thermodynamics gives $K = e^{-\Delta G/RT}$ and it follows that $\frac{P_1Z_1}{P_2Z_2} = e^{\Delta S/R}$

The product PZ must involve an entropy term and the collision theory provides no explanation of this.

1.5 Absolute Reaction Rate Theory[17]

The aim of this theory is to predict the values of rate constants from a consideration of both concentration and configuration. The main assumption made is that an equilibrium exists at all times between the activated complex and/

/and the reactants. It treats the activated complex as a normal molecule except that it has no vibrational degree of freedom in the direction of the reaction co-ordinate.

If we consider the formation of the activated complex M^{*},

$$X + Y \rightleftharpoons M^{*} \longrightarrow \text{products.}$$

the reaction rate can be expressed as the product of the concentration of the activated complex and the frequency of crossing the energy barrier. This may be expressed:

$$\text{Rate of Reaction} = C_{\neq}' \frac{\overline{\nu}}{\delta}$$

where $C_{\neq}'$ is the number of complexes in unit volume along a distance δ at the top of the barrier and $\overline{\nu}$ is assumed as the mean velocity of crossing. Treating the complex as a normal molecule;

$$C_{\neq}' = C_{\neq} \frac{(2\pi M^{*} kT)^{\frac{1}{2}}}{h} \delta$$

where $C_{\neq}$ is the concentration, M^{*} the effective mass and $\frac{(2\pi M^{*} kT)^{\frac{1}{2}}}{h}\delta$ is the partition function for translation in the reaction co-ordinate of the complex. By the kinetic theory $\overline{\nu}$ is $\left(\frac{2kT}{M^{*}}\right)^{\frac{1}{2}}$, but allowing for the fact that only the complexes moving in one direction lead to reaction, the reaction rate may be expressed:

$$\text{Rate} = \frac{C_{\neq} (2\pi M^{*} kT)^{\frac{1}{2}}}{2h} \delta \left(\frac{2kT}{\pi M^{*}}\right)^{\frac{1}{2}} \frac{1}{\delta}$$

$$= C_{\neq} \frac{kT}{h}$$

It should be noted that the actual length of δ need not be specified as it does not appear in the final expression for the reaction rate. We have assumed that all complexes crossing the barrier complete the reaction. As this is not always the case a transmission coefficient is introduced. For many reactions it can be taken as unity.

Since/

Since the reaction rate = $k' CxCy$ the following expression may be written:

$$k' = \frac{kT}{h} \frac{C_{\neq}}{CxCy} = \frac{kT}{h} \bar{K}^{\neq}$$

where $\bar{K}^{\neq}$ is the equilibrium constant for the activation process. The following thermodynamic relationship may then be introduced.

$$\Delta G^{\neq} = -RT \ln . \bar{K}^{\neq}$$

Therefore $\bar{K}^{\neq} = e^{-\Delta G^{\neq}/RT}$

Now $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$

Therefore $k' = \frac{kT}{h} e^{\Delta S^{\neq}/R} e^{-\Delta H^{\neq}/RT}$

Now $\frac{\text{Eact (experimental)}}{RT^2} = \frac{d \ln k'}{dT} = \frac{1}{T} + \frac{d \ln \bar{K}c^{\neq}}{dT}$

Therefore $E \text{ (experimental)} = RT + \Delta U^{\neq} = RT + \Delta H^{\neq} - P\Delta V^{\neq}$

The symbol $\Delta U^{\neq}$ represents the increase in internal energy for the activation process and $\Delta V^{\neq}$ is the accompanying increase in volume.

Now $P\Delta V^{\neq} = \Delta n^{\neq} RT$

For $\Delta n^{\neq} = -1$ as in $X + Y \longrightarrow M^{*}$

$$k = e^{2} \frac{kT}{h} e^{\Delta Sc^{\neq}/R} e^{-E \text{(experimental)}/RT}$$

The experimental A factor is seen to be $e^{2} \frac{kT}{h} e^{\Delta Sc^{\neq}/R}$.

The symbol $\Delta Sc^{\neq}$ represents the entropy of activation at constant concentration and as it is slightly temperature dependent so is the A factor. By splitting the entropy term into its vibrational, rotational and translational components the A factor may be calculated.

1.6 Comparison of Collisional and Absolute Theories

Using statistical thermodynamics we may express $\bar{K}^{\neq}$ the equilibrium constant for the activation process $X + Y \rightleftharpoons M^{*}$

as $\bar{K}^{\neq} = \frac{Q^{\neq}}{QxQy} e^{-E/RT}$ (Q = partition function)

Substituting this expression for $\bar{K}^{\ddagger}$ into the equation $k' = \frac{kT}{h}.\bar{K}^{\ddagger}$ the following equation is obtained. $k' = \frac{kT}{h}\frac{Q^{\ddagger}}{QxQy}e^{-E/RT}$

Consideration of the Arrhenius expression, $k' = A\,e^{-E/RT}$, gives $A = \frac{kT}{h}\frac{Q^{\ddagger}}{QxQy}$

On the assumption that X and Y have no vibrational or rotational degrees of freedom, i.e. X and Y are atoms, this equation may be written:

$$A = \frac{\frac{kT}{h}.\frac{(2\pi(Mx+My)kT)^{3/2}}{h^3}.\frac{8\pi kT}{h^2}.\frac{MxMy}{Mx+My}.r_{xy}^2}{\frac{(2\pi MxkT)^{3/2}}{h^3}.\frac{(2\pi MykT)^{3/2}}{h^3}}$$

where Mx = mass of X, My = mass of Y and r_{xy} = distance between X and Y in the complex. The value of $Q^{\ddagger}$ is the product of $Q^{\ddagger}$(translational) and $Q^{\ddagger}$(rotational). No vibrational term is included as the activated complex has only one and that is included in the factor kT/h.

The above expression for A reduces to $r_{xy}^2\left(8\pi kT\,\frac{(Mx+My)}{MxMy}\right)^{\frac{1}{2}}$ which is identical with the collisional expression (page 6). Agreement is not obtained for reactions involving molecules. This may be seen if we denote the contribution of a single translational, rotational and vibrational degree of freedom as q_t, q_r and q_v respectively. The total partition function for a molecule may then be expressed as $Q = q_t^{t'}.q_r^{r'}.q_v^{v'}$ where t', r' and v' are the number of degrees of freedom contributing. For the reaction of two atoms X and Y .

$$Qx = q_{tx}^3,\ Qy = q_{ty}^3 \text{ and } Q = q_t^3.q_r^2$$

If it is assumed that the partition function for each type of energy is made up of equal terms, one for each degree of freedom, we obtain:

$$k' = \frac{kT}{h}\frac{q_r^2}{q_t^3}e^{-E/RT}$$

In the general case where X and Y contain Nx and Ny atoms respectively and are both non-linear $Qx = q_t^3 . q_r^3 . q_v^{(3Nx-6)}$, $Qy = q_t^3 . q_r^3 . q_v^{3Ny-6}$ and $Q^{\ddagger} = q_t^3 . q_r^3 . q_v^{3(Nx+Ny)-7}$

The expression for k' is found to be $k' = \frac{kT}{h} \frac{q_v^5}{q_t^3 q_r^3} e^{-E/RT}$

This differs from the collision theory expression by the factor $(\frac{q_v}{q_r})^5$. Laidler[18], taking q_v as unity and q_r between 10 and 100, shows that the term $(q_v/q_r)^5$ can be as low as 10^{-5} to 10^{-10} and hence the reaction rate between complex molecules can be slower by this factor than the rate estimated from collision theory.

1.7 Temperature Dependence of A and E

From the collision theory expression, $A = r_{xy} \left(\frac{8\pi kT(Mx + My)}{MxMy}\right)^{\frac{1}{2}}$, the A factor is seen to be proportional to temperature raised to the power one half. In the absolute reaction rate theory the power to which T is raised is dependent on the form of the partition functions of the reactants and the activated complex. The Arrhenius equation should therefore be written $k = aT^n e^{-E/RT}$. The experimental fact that plots of log k against 1/T appear linear is due to the stronger temperature dependence of the exponential part than that of the pre-exponential part. Hinshelwood[19] has shown that the simple exponential dependence of E was only accurate for systems in which the energy was distributed in two square terms, as in the motion of two bodies along their line of centres or a vibration of a bond. For more complex molecules the fraction with energy greater than E distributed among n square terms is given by :

$$\frac{Ne}{No} = \left[\left(\frac{E}{RT}\right)^{(\frac{1}{2}n-1)} / (\tfrac{1}{2}n-1)! \right] e^{-E/RT}$$

Plotted in the Arrhenius form this equation gives an apparent activation energy;

$$Eapp = E - (\tfrac{1}{2}n-1)RT \text{ and } Aapp = \frac{A}{(\frac{1}{2}n-1)!}$$

The variation of Ea over an experimental range is generally too small to be detected but it has been pointed out[20] that experimental values of Ea may lead to values of E at 0°K which are seriously in error. For bimolecular metathetical reactions the violence of collision is all important and hence the assumption that the energy is distributed in two square terms will be nearly correct.

I.2 Complex Chemical Reactions

The kinetic theories dealt with above have been concerned with the rates of elementary reactions. Gas phase kinetic studies have shown that most reactions are the result of a series of well defined elementary reactions. In describing a complex gas reaction it is normal to list these elementary reactions and describe this series of reactions as the reaction mechanism. It is common for species to appear in the mechanism which do not belong to either products or reactants and these are known as intermediates. These intermediates may be stable molecules which undergo chemical attack or they may decompose unimolecularly at the reaction temperature. Experiments[21, 22, 23] have shown that a common type of intermediate is not a stable species but a free radical. This is an electron deficient species produced from a stable molecule by the loss of a group or atom generally in an abstraction reaction by a body which is itself electron deficient. The existance of free radicals was first confirmed by Paneth[21,22] and Taylor and Jones[23]. The presence of atoms in gas phase reactions first proposed by Nernst[6], Polanyi[5], etc., has been amply confirmed by subsequent work and the atomic chain mechanism suggested by these workers has proved to be the reaction route in the halogenation reaction of the hydrocarbons.

2.1 Determination of the Rate Constants and Arrhenius Parameters of Elementary Reactions

Once/

Once the intermediates of a complex reaction have been characterised it is possible to construct a mechanism which will explain the reaction products and consideration of the thermodynamics and kinetics of the mechanism can then check if this reaction path is feasible. Consider the following hypothetical chain reaction.

$$X_2 \longrightarrow 2X \qquad 1$$

$$X + AB \longrightarrow XA + B \qquad 2$$

$$B + X_2 \longrightarrow BX + X \qquad 3$$

$$X + X \longrightarrow X_2 \qquad 4$$

A value for the rate constant of reaction 2, k_2, may be required. The reaction rate is given by, Rate (2) = k_2 (AB)(X).

In order to determine k_2 we must know,

1) The rate of removal of AB or production of XA,

2) The concentration of AB and

3) The concentration of X

Normally 1) and 2) can be obtained by experiment while 3) is difficult if not impossible to measure. In order to resolve the problem of measurement of intermediate concentrations the steady state method was developed. This makes the assumption that the concentrations of the intermediates are so small that they are negligible in comparison with those of reactants and products. The rate of change of the intermediate can then also be considered as negligible and taken as equal to zero.

It is then possible to write

(a) $$\frac{d(X)}{dt} = 0 = 2k_1(X_2) - k_2(X)(AB) + k_3(B)(X_2) - k_4(X)^2$$

and (b) $$\frac{d(B)}{dt} = 0 = k_2(X)(AB) - k_3(B)(X_2)$$

Adding/

Adding (a) and (b) we obtain $2k_1(X_2) - k_4(X)^2 = 0$

Therefore $(X) = \left\{\frac{2k_1(X_2)}{k_4}\right\}^{\frac{1}{2}}$

This equation can be used to check the validity of the stationary state method for any particular reaction if values of k_1 and k_4 are known. By rearrangement $\frac{(X)}{(X_2)} = \left\{\frac{2k_1}{k_4(X_2)}\right\}^{\frac{1}{2}}$. If (X) is to be less than 1% of (X_2) the expression $\left\{\frac{2k_1}{k_4(X_2)}\right\}^{\frac{1}{2}}$ must be less than 0.01. This implies that $2k_1$ is less than $10^{-4}k_4(X_2)$.

The rate of production of XA is given by $R_2 = k_2(X)(AB) = k_2(AB)\left\{\frac{2k_1(X_2)}{k_4}\right\}^{\frac{1}{2}}$

If the species X_2 and X are in equilibrium, with equilibrium constant $\bar{K}_x$, the rate given above may be expressed

$$R = k_2 \bar{K}_x^{\frac{1}{2}}(AB)(X_2)^{\frac{1}{2}}$$

This procedure can give incorrect results if the equilibrium $X_2 \rightleftharpoons 2X$ is not obtained because of the rapid removal of X by reaction 2. Benson and Buss[24] have shown that this is so for the chlorination and bromination of certain hydrocarbons. A second possible source of error is the nature of the termination step (4). In the above example the recombination of X was chosen but the following reactions could also have been of importance.

$$B + X \longrightarrow BX \qquad 5$$

$$B + B \longrightarrow B_2 \qquad 6$$

If these reactions are included the rate expression derived above will no longer hold. These disadvantages can be avoided by the use of a competitive technique. If reaction 2 is allowed to compete with 2^1:

$$X + AB^1 \longrightarrow XA + B^1 \qquad 2^1$$

then $\frac{R_2^1}{R_2} = \frac{k_2^1(X)(AB^1)}{k_2(X)(AB)} = \frac{k_2^1}{k_2}\frac{(AB^1)}{(AB)}$

This method yields rate constant ratios and it is necessary to measure one absolute/

/absolute rate constant and then relate others to it by the competitive method. This method has proved of great value in halogenation studies[25, 26, 27].

I.3 Halogenation Reactions

A detailed review of the reactions of Cl, Br and F with hydrocarbons has recently been published by Fettis and Knox[28] and it is proposed to review here only the reactions of iodine in the gas phase along with related reactions e.g. decomposition of iodides.

3.1 Iodination of Hydrogen and the decomposition of HI

Bodenstein[1, 2, 29] and his co-workers studied the reaction of iodine with hydrogen and the decomposition of HI. They found that the reactions fitted the second order rate laws,

$$\text{Rate of HI formation} = k_f(I_2)(H_2)$$

$$\text{Rate of decomposition} = k_d(HI)^2$$

Bodenstein did not express his rate constants in the form of an Arrhenius equation but showed that they fitted equations of the type

$$\log k = \frac{A}{T} + B \log T + C \qquad 1$$

$$\log k = \frac{A}{T} + B \log T + CT + D \qquad 2$$

He chose to fit his data to an equation of type 2 as this form appeared to fit the equilibrium constant data for the H_2/I_2 system. From this work the accepted reaction mechanism became

$$H_2 + I_2 \rightleftharpoons \begin{matrix} H \cdots H \\ \vdots \quad \vdots \\ I \cdots I \end{matrix} \rightleftharpoons 2HI$$

A large number of other workers have re-examined the H_2/I_2[30-34] system and a number have studied the D_2/I_2[34-37] system. The studies involved both static and flow systems and analysis of the data was generally based on the Bodenstein mechanism. The mean activation energy found for the formation of HI was 40 kcal $mole^{-1}$ and the reaction was found to be homogeneous. Kassel[38] analysed Bodenstein's/

/Bodenstein's data and showed that it differed in a systematic fashion from 1 but in a random way from 2, the variation was within experimental error. Kassel also showed that Bodenstein's data could not be fitted in a satisfactory manner to an Arrhenius plot. Consideration of the different temperature regions in which Bodenstein worked gave a variable A factor and an activation energy which increased with temperature at a rate of 35 cal deg^{-1}.

Benson and Srinivasan[39] suggested that an atomic mechanism might be important in the reaction of iodine with hydrogen. Their mechanism was:

$$I_2 + M \underset{k_3}{\overset{k_2}{\rightleftharpoons}} 2I + M$$

$$I + H_2 \underset{k_5}{\overset{k_4}{\rightleftharpoons}} HI + H$$

$$H + I_2 \underset{k_7}{\overset{k_6}{\rightleftharpoons}} HI + I$$

Applying the stationary state method and neglecting the slower back reaction they obtained:

$$\frac{d(HI)}{dt} = \frac{2k_4(H_2)(I_2)^{\frac{1}{2}}\left(\frac{k_2}{k_3}\right)^{\frac{1}{2}}}{1 + k_5\,(HI)/k_6(I_2)}$$

Assuming that $E_6 \leq E_5$ it was likely that $k_5 < k_6$ and in the initial stages when $(I_2) > (HI)$

$$\frac{d(HI)}{dt} = 2k_4\,(H_2)(I_2)^{\frac{1}{2}}\,\bar{K}_{I_2}^{\frac{1}{2}}$$

For the bimolecular reaction $\frac{d(HI)}{dt} = k_b(H_2)(I_2)$ so that Benson and Srinivasan obtained for the overall rate expression

$$\frac{d(HI)}{dt} = k_b(H_2)(I_2)\left\{1 + \frac{2k_4(\bar{K}_{I_2})^{\frac{1}{2}}}{k_b(I_2)^{\frac{1}{2}}}\right\}$$

They attempted to estimate the ratio k_4/k_b in the following manner. In terms of transition state theory

$$\frac{k_4}{k_b} = \frac{Q(I_2)\,Q(H_2I^*)}{Q(I)\,Q(H_2I_2^*)}\ \exp.\left\{\frac{E^\circ_b - E^\circ_4}{RT}\right\}$$

/if transmission coefficients are assumed unity. Taking the activated complex of the atomic mechanism as linear and of length 0.97Å and that of the molecular mechanism as planar and symmetrical and of dimensions H - H = 0.97Å, H-I = 1.75Å and I-I = 2.95Å, they reduced the above expression to the following.

$$\frac{k_4}{k_b} = 6 \left\{ \frac{Q_{el}(H_2I^*)}{2} \right\} K(vib) \exp. \left(\frac{E_b - E_4}{RT} \right)$$

No attempt was made to evaluate Q(vib) or the zero point energies of the species. Instead it was assumed that $E^\circ_b - E^\circ_4 = E_b - E_4$. Further approximations which favour k_b reduced the expression to:

$$\frac{k_4}{k_b} \approx e^{(E_b - E_4)/RT}$$

Using a value between 39 and 41 kcal mole^{-1} for E_b and estimating E_4 to be in the range 32.8 to 35 kcal mole^{-1} Benson and Srinivasan obtained the range of $E_b - E_4$ as 4.0 to 8.2 kcal mole^{-1} which led them to the view that atomic reaction would be important at low pressures and high temperatures. Lewis and Rideal[31] had suggested that atomic reaction might be important in this system. However they had considered the reaction $I_3 + H_2 \longrightarrow 2HI + I$ to be more important than $I + H_2 \longrightarrow IH + H$. Bodenstein and Jost[40] showed that the work of Lewis and Rideal was inaccurate. Rosenbaum and Hogness[41] studied the conversion of para to ortho hydrogen in the presence of I_2. They worked with mixtures of I_2, H_2 and HI at equilibrium and hoped to show that the rates of the bimolecular reactions were identical with those measured far from equilibrium. The rates which they obtained were almost twice the values expected and this they explained by assuming that the paramagnetic iodine atom could cause the ortho-para conversion when in collision with a hydrogen molecule, i.e. $pH_2 + I \longrightarrow oH_2 + I$. The data however gives an activation energy of 24 kcal mole^{-1} for this process and it has been shown that this type of conversion has a very small positive or negative temperature dependence.[42]

In/

/In an effort to determine the relative importance of the atomic and molecular paths Sullivan[43,44,45] carried out a series of experiments and found the best fit for his theoretical expression to the data by a computer. Sullivan took as the mechanism:

$$I_2 \rightleftharpoons 2I \qquad (1)$$

$$H_2 + I_2 \longrightarrow 2HI \qquad (2)$$

$$2(HI) \longrightarrow H_2 + I_2 \qquad (3)$$

$$I + H_2 \longrightarrow HI + H \qquad (4)$$

$$H + HI \longrightarrow H_2 + I \qquad (5)$$

$$I + HI \longrightarrow H + I_2 \qquad (6)$$

Taking $\frac{d(H)}{dt} = o$ he applied the stationary state method and obtained the following rate equation:

$$\frac{d(HI)}{dt} = 2k_1((H_2)(I_2) - K(HI)^2)\left[1 + K_d \frac{k_3}{k_1(I_2)^{\frac{1}{2}}}\left[1 + \frac{k_4(HI)}{k_5(I_2)}\right]^{-1}\right]$$

where K is the equilibrium constant for the overall reaction and K_d is that for the iodine dissociation. Using statistical methods, values for k_1, k_3 and k_4/k_5 were determined. Sullivan[45] explained the results of Rosenbaum[41] by applying these values to his results. Sullivan's results therefore indicate that Benson and Srinivasan[39] are correct and that the percentage importance of the atomic mechanism is 10%, 27% and 95% at 633°K, 738°K and 800°K respectively. Graven[33] claimed that his results indicated that the bimolecular reaction was paramount in the temperature range 873°K to 1048°K. Horie, Ishi and Amano[46] have shown that Graven's results fit the integrated rate equation obtained by considering both the atomic and molecular paths.

3.2 Iodination of Hydrocarbons

Despite the great interest in the reaction of iodine with hydrogen it is only since the start of the present research work that the results of the reactions/

/reactions of iodine with hydrocarbons in the gas phase have been published and as yet the results are limited in comparison with the data for the similar reactions of chlorine and bromine.

Propane

The kinetics and thermodynamics of the reaction of iodine with propane have been studied by Benson and Nangia[47/48] in the temperature range 308°C to 340°C. The reaction mechanism was assumed to be:

$$I_2 + M \rightleftharpoons 2I + M \quad \text{(at equilibrium)}$$

$$C_3H_8 + I \underset{2}{\overset{1}{\rightleftharpoons}} C_3H_7 + HI$$

$$C_3H_7 + I_2 \underset{4}{\overset{3}{\rightleftharpoons}} iPrI + I$$

$$iPrI \underset{6}{\overset{5}{\rightleftharpoons}} C_3H_6 + HI$$

The overall reaction was:

$$C_3H_8 + I_2 = C_3H_6 + 2HI$$

and it was followed manometrically. Benson and Nangia deduced the rate equation

$$\frac{(C_3H_8)(1-B)}{2\left(\frac{-d(I_2)^{\frac{1}{2}}}{dt}\right)} = \frac{1}{k_1\bar{K}_I}^{\frac{1}{2}} + \frac{k_2k_4}{k_3k_5k_1\bar{K}_{I_2}^{\frac{1}{2}}}\frac{(HI)(I)}{(I_2)} + \frac{k_2(HI)}{k_3k_1\bar{K}_{I_2}^{\frac{1}{2}}(I_2)}$$

where $B = \frac{(C_3H_6)(HI)^2}{K(C_3H_8)(I_2)}$, $\bar{K}_{I_2}$ = equilibrium constant for I_2 dissociation and K = overall reaction equilibrium constant. The expression $\frac{k_3k_5k_1}{k_2k_4}$ was replaced by k_6K.

Regrouping the expression gave:

$$Z = \frac{1}{k_1\bar{K}_{I_2}^{\frac{1}{2}}}\left[1 + \frac{k_2}{k_3}\frac{(HI)}{(I_2)}\right] + \frac{1}{k_6K}\frac{(HI)}{(I_2)^{\frac{1}{2}}}$$

Benson and Nangia using values of K[48] and k_6[49], obtained from previous work, plotted $(Z - (HI)/k_6K(I_2)^{\frac{1}{2}})$ against $(HI)/(I_2)$ and obtained straight lines of slope $k_1\bar{K}_{I_2}^{\frac{1}{2}}$ and intercept k_2/k_3. The experimental values of k_1 fitted the/

/the expression log k_1 (cc/mole-sec) = 14.53 ± 0.36 - (25.5 ± 1.0)/2.303RT. The constant k_1 is for iodine atom attack on the whole molecule and by approximate calculation based on the assumption that the activation energy difference between attack on the primary and secondary hydrogen atoms was equal to the bond strength difference between these positions they deduced that for attack by iodine atoms at the secondary position.

$$E_{act} = 25.0 \pm 1 \text{ kcal mole}^{-1}$$

and $$\log A = 14.22 \pm 0.36$$

The ratio k_2/k_3 was found to be near 2 and disagreed with this ratio obtained for 12 similar systems[47]. By assuming $k_2/k_3.(HI)/(I_2) \sim 0$ during the first 15% reaction and plotting Z against $(HI)/(I_2)^{\frac{1}{2}}$ a value for k_6 could be obtained from the slope of the straight line plot. The expression log k_6 (cc/mole-sec) = 10.5 - 23,700/2.303RT was found to hold for the data. The absolute values are in disagreement with Benson and Bose[49] by a factor of 2.5.

The study of the overall equilibrium[48] yielded values for K_p which fitted the expression log K_p (atm) = (8.09 ± 0.15) - (27.88 ± 0.40)/2.303RT in excellent agreement with K_p values calculated from independent thermodynamic data.

Isobutane

Studies similar to those for the I_2/propane system have been carried out by Benson and Teranishi[50,51] for the reaction of iodine with isobutane. The reaction was followed by measuring, by means of a spectrophotometer, the rate of removal of iodine and the mechanism was considered identical with that of the propane reaction. The rate law was expressed in the manner

$$Z = a_1 + a_2 \cdot \frac{(HI)}{(I_2)^{\frac{1}{2}}} + \frac{b(HI)}{(I_2)}$$

where/

/where $a_1 = \frac{1}{k_1(K_{I_2}^{\frac{1}{2}})}$, $a_2 = \frac{1}{k_6 K}$ and $b = \frac{k_2}{k_3 k_1 K_{I_2}^{\frac{1}{2}}} = a_1 \frac{k_2}{k_3}$.

Benson[52] from a previous study of the addition of HI to isobutene obtained a value for k_6 and the equilibrium constant K was determined in this work[51]. Hence a value for a_2 could be calculated and values for a_1 and b were determined from any two points on the plot of Z against $(HI)/(I_2)^{\frac{1}{2}}$. Values for k_1 and k_2/k_3 were then readily estimated. From an Arrhenius plot of k_1:

$$\log k_1 \text{ (cc/mole-sec)} = 13.88 \pm 0.15 - \frac{21400 \pm 500}{2.303\ RT}$$

The ratio of k_2/k_3 was found to be 0.226 and 0.251 at 525.4°K and 582.8°K respectively, this being the temperature range of the study. Owing to the difference in bond strength between the tertiary hydrogen and the primary hydrogen in the isobutane molecule the expression for k_1 can be considered to hold for the attack of an iodine atom at the tertiary position. The equilibrium studies[51] gave the following expression.

$$\log K_p(\text{atm}) = +\ 8.13 - \frac{25{,}900 \pm 300}{2.303\ RT}$$

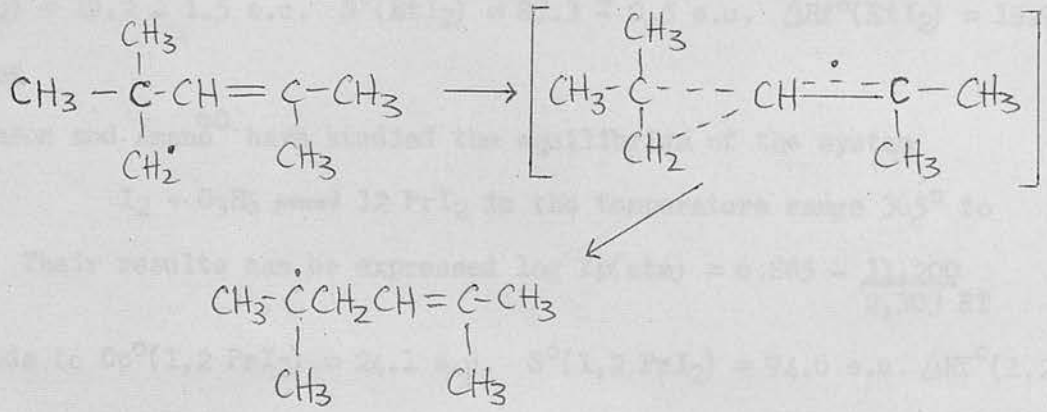
When K_p is plotted against 1/T this gives a line parallel to, but 10% above, the theoretical plot based on independent thermodynamic data.

It should be noted that owing to the specific nature of the iodine atom attack on the hydrocarbon the above kinetic results give an excellent method for the estimation of the C-H bond strengths in hydrocarbons. It is proposed to return to this topic in a another section of this thesis.

3.3 <u>High Temperature Studies</u>

Raley and his co-workers[53-55] have examined the products of the reaction of iodine with a number of hydrocarbons in a flow system over the temperature range 600-685°C. The ratio I_2/Hydrocarbon and the contact time of the reactants were varied to a limited extent. Primary products could be explained by the atomic mechanism discussed above. The reactions were carried/

/carried to large conversions and secondary products were found which could be explained on the basis of further abstraction reactions by iodine atoms. They were able to deduce that the abstraction of an allylic hydrogen atom has an activation energy considerably less than that for a hydrogen atom in a saturated hydrocarbon. Aromatic products were obtained with a number of aliphatic hydrocarbons. Propane yielded benzene, isobutane gave p-xylene and n-butane had o-xylene as a product. The yields of these aromatic compounds were in the region of 3 to 4%. By showing that aliphatic hydrocarbons containing six and eight carbon atoms were converted to aromatics[54] the authors suggest that the aromatics were produced from the lower hydrocarbons by means of a dimerisation followed by repeated abstraction reactions. As hydrogen was obtained as a minor product (~1%) molecular elimination of hydrogen may also be involved in the aromatisation mechanism. Evidence[55] for radical rearrangements, involving 1-2 vinyl group migration in the presence of iodine, was also found, i.e.



Cyclopropane

The reaction of iodine with cyclopropane was studied by Ogg and Priest[56] in 1939 and their data re-examined by Benson[57] in 1961. The mechanism proposed by Ogg was $I_2 \underset{2}{\overset{1}{\rightleftharpoons}} 2I$

$$I + \text{cyclo } C_3H_6 \underset{4}{\overset{3}{\rightleftharpoons}} ICH_2CH_2CH_2$$

$$ICH_2CH_2CH_2 + I_2 \underset{6}{\overset{5}{\rightleftharpoons}} I(CH_2)_3I + I$$

Using/

/Using thermodynamic data and information about iodine atom attack on iodides Benson was able to deduce $\log k_6 = 11.0 - \frac{19,500}{2,303\ RT}$

$$\log k_5 = 9.5 - \frac{500}{2,303\ RT}$$

The di-iodide is not a stable species and decomposes to give propylene. Benson proposed that the mechanism leading to propylene was

$$I + CH_3CH_2CH_2I \longrightarrow CH_3CHCH_2I + HI$$

$$CH_3CHCH_2I \longrightarrow CH_3CH = CH_2 + I$$

3.4 Reactions of Iodine with Olefines

Ethylene

The equilibrium $I_2 + C_2H_4 \rightleftharpoons C_2H_4I_2$ has been studied by a number of workers[58-60]. The temperature range covered has been 323° to 475.8°K. The results were in good agreement giving the equilibrium constant as

$\log K_p(atm) = 6.885 - \frac{11,500}{2,303\ RT}$ which led to

$Cp^\circ(EtI_2) = 19.2 \pm 1.5$ e.u. $S^\circ(EtI_2) = 83.3 \pm 0.5$ e.u. $\Delta Hf^\circ(EtI_2) = 15.9 \pm 0.2$ kcal

Propylene

Benson and Amano[60] have studied the equilibrium of the system

$I_2 + C_3H_6 \rightleftharpoons 12\ PrI_2$ in the temperature range 365° to 448°K. Their results can be expressed $\log Kp(atm) = 6.885 - \frac{11,200}{2,303\ RT}$

This leads to $Cp^\circ(1,2\ PrI_2) = 24.1$ e.u. $S^\circ(1,2\ PrI_2) = 94.6$ e.u. $\Delta Hf^\circ(1,2\ PrI_2) = 8.6$ kcal/mole

Iodine catalysed positional isomerisation of Olefines

Butene 1 and Butene 2

The reactions of iodine with butene-1 and butene-2, in the gas phase, have given no indication of the di-iodide having any measurable stability. Interest in the systems has been centered on the isomerisation reactions catalysed by iodine atoms. Benson and Bose[61] examined the butene-1-butene-2 and/

/and the cis-trans butene-2 equilibria. They proposed as the mechanism for the butene-1 conversion the following.

$$CH_3\text{-}CH_2\text{-}CH{=}CH_2 \xrightarrow{I} CH_3\text{-}CH \text{====} CH \text{====} CH_2 + HI$$

The reverse of this reaction can then lead to butene-1 or butene-2. The path proposed for the cis-trans isomerisation involved the addition of an iodine atom to the double bond to produce an iodoalkyl radical in which rotation about the $C_2 - C_3$ bond is possible. Benson, Bose and Nangia[62] studied the kinetics of the butene -1 conversion to butene-2 in a static system over the temperature range 204° to 252°C. Taking the attack of the iodine atom as the rate determining step they deduced:

$$-\frac{d(B_1)}{dt} = k_1(B_1)(I) - k_2(B2)(I)$$

$$= (B_1 - \frac{B_1^{\circ}}{1 + K_{12}})(k_1 + k_2)(I)$$

B_1 = butene-1, B_2 = butene-2, B_1° = Initial concentration of B_1, $K_{12} = k_1/k_2$. Integration and rearrangement of the above equation gave:

$$k_1 = \frac{\frac{K_{12}}{(1 + K_{12})}}{K I_2^{\frac{1}{2}} (I_2)^{\frac{1}{2}} t} \ln\left[\left(\frac{(B_1)}{(B_1^{\circ})} - \frac{1}{1 + K_{12}}\right)\left(\frac{1 + K_{12}}{K_{12}}\right)\right]$$

An Arrhenius plot of the data for k_1 fitted the line:

$$\log k_1 \text{ (cc/mole-sec)} = 12.53 - \frac{(13,200 \pm 400)}{2,303\ RT}$$

Benson, Golden and Egger[63,64] have repeated the above work and have also measured the rate of the cis-trans isomerisation[65]. For the equilibrium studies their results are in agreement with the previous study and with other studies of these equilibria[66]. They were able to detect the presence of small quantities of butadiene in the equilibrium mixture and they proposed the following mechanism for its formation.

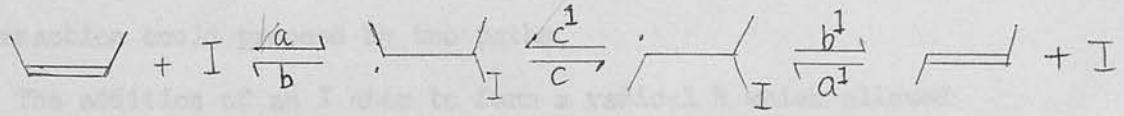
$$CH_2{=}CH\text{-}CH_2\text{-}CH_3 + I \longrightarrow CH_2 \text{====} CH \text{====} CH\text{-}CH_3 + HI$$

$$\downarrow I_2$$

$$1,3 \text{ butadiene} + HI \longleftarrow CH_2{=}CH\text{-}CHI\text{-}CH_3 + I$$

The values for the thermodynamic functions of the isomers determined from the above studies indicate that previously accepted values[67] have been slightly in error. In the kinetic study[64] the activation energy for the butene-1 isomerisation was found to be 12.4 ± 0.6 kcal mole^{-1} and the value of log.A$_1$ to be 12.0 ± 0.3. From these results it was deduced that the allylic resonance energy, (defined as the difference in energy between a carbon - hydrogen bond conjugated with a double bond and a similar bond in a saturated hydrocarbon), was 12.6 kcal mole^{-1}.

The mechanism of the cis-trans isomerisation was assumed to be[65]



Application of the stationary state method gave:

$$-\frac{d(Bc)}{dt} = \frac{Kab\ k_c(Bc)(I)}{1 + Kcb + Kc^1b^1}\left[1 - \frac{k_c^1 Ka^1 b^1 (Bt)}{k_c Kab (Bc)}\right]$$

where Bc = cis butene-2, Bt = trans butene-2 and $Kab = \frac{ka}{kb}$ etc.

Benson[65] indicates that the expression $\frac{Kabkc}{1+Kcb+Kc^1b^1}$, which is equivalent to the determined rate constant (k_1), can be simplified when the following conditions hold.

1) Kcb and $Kc^1b^1 \ll 1$ then $k_1 = Kabkc$

2) Kcb and $Kc^1b^1 \gg 1$ then $\frac{1}{4}k_a < k_1 < \frac{3}{4}k_a$

3) $Kcb = Kc^1b^1 \sim 1$ then $k_1 = \frac{1}{3}k_a$

By using thermodynamic data, substituting unimolecular Arrhenius parameters and calculating k_c by the formula $k_c = \frac{RT}{h} Kc^* e^{-Eo^*/RT}$ it was possible for Benson to obtain approximate values for the rate of conversion in each of the above three cases.

1) $k_1 = 10^{8.4}\ 10^{-9.0/2.303RT}$

2) $k_1 = 10^{9.5}\ 10^{-7.5/2.303RT}$

3) $k_1 = 10^{9.6}\ 10^{-7.5/2.303RT}$

The/

The experimental value found for k_1 was $10^{8.5 \pm 0.3}\ 10^{-9.4/2.303RT}$ which fits case 1. Hence the determined rate was that for rotation about the single bond.

Back and Cvetanovic[68,69] have studied these isomerisation reactions in a photochemical experiment at 65°C using light from three spectral regions.

a) $\lambda > 5{,}000A^\circ$ b) $\lambda < 5{,}000A^\circ$ c) $\lambda = 2{,}537A^\circ$

In some runs N_2 and O_2 were added to the system.

The effect of the variables proved to be complex. Back and Cvetanovic rationalised the results for the cis-trans isomerisation[68] by assuming that the reaction could proceed by two paths,

a) The addition of an I atom to form a radical R which allowed rotation about the position of the double bond.

b) The combination of a cis butene 2 molecule with an iodine atom to form a complex in which rotation was not allowed but which could react in three ways. 1) To form the radical R.
2) To decompose to give reactants.
3) To react with an iodine atom to form a di-iodide which then decomposed to give cis and trans isomers.

Path a) is equivalent to the Benson mechanism[65]. The complex formed in b) is considered by Cvetanovic to be similar to those proposed by Porter[79] to explain third body efficiences in iodine atom recombinations. The butene-1 to-2 isomerisation was also studied[69] and butadiene was detected as a product. Cvetanovic ruled out a direct iodine atom abstraction reaction as its rate with ground state iodine atoms ($\lambda > 5000A^\circ$) at 65°C could not account for the rate of formation of butadiene. Two possible paths are suggested:

(a) $I + C_4H_8 \longrightarrow (C_4H_8I)$

$I + (C_4H_8I) \longrightarrow C_4H_7I + HI$

A/

/A repetition of this reaction on C_4H_7I would lead to butadiene

(b) $C{:}I + I \longrightarrow CI_2 \longrightarrow C_4H_6 + 2HI$

Studies carried out with deuterated butadiene lead these workers to suggest that mechanism (a) is the most likely route.

3.5 Recombination of Iodine Atoms

The recombination of iodine atoms in the gas phase has been studied by a large number of workers[70-80]. All the experiments have shown that the recombination requires a third body so that the rate of formation of I_2 may be expressed $d(I_2)/dt = k(I)^2(M)$.

Russel and Simons[73] evaluated a number of substances as third bodies and suggested that their efficiency could be related to the magnitude of their intermolecular force field. Christie[72] showed that the iodine molecule was a more efficient third body than any of the previously tested organic compounds. Rabinowitch[70] explained this by considering the detailed mechanism of recombination. In detail there exist two possible paths for recombination

A. $I + I \rightleftharpoons I_2^*$; $I_2^* + M \longrightarrow I_2 + M$

B. $M + I \rightleftharpoons IM$; $IM + I \longrightarrow M + I_2$

The greater efficiency of I_2 cannot be explained by A. Rollefson and Eyring[71] have shown that I_3 has considerable stability and this would assist mechanism B when M is I_2. Porter and Smith[79,80] have pointed out that the magnitude of the negative temperature coefficient found for the recombinations cannot be explained on the basis of Van der Walls forces. They suggest that the efficiency of a third body depends on its ability to form a complex with the iodine atom and these complexes may be of the charge transfer type found in organic solutions of iodine.

3.6 Pyrolysis of Iodides

The thermal decompositions of iodides have proved difficult to interpret owing/

/owing to their complex nature. The early work of Polanyi[81], Jones[82] and Ogg[83,84] was based on the assumption that the primary step was the breaking of the R-I bond to give an iodine atom and an alkyl radical. Steacie[85] has reviewed the early work indicating inadequacies in the data without suggesting an alternative mechanism. Benson[86] has reviewed the topic in the light of modern knowledge and he has been able to indicate the mode of decomposition of a number of iodides.

Ethyl Iodide

Benson and Bose[87] examined the decomposition of ethyl iodide in the temperature range 330° to 392°C. The products detected were ethane, iodine and ethylene in equimolar quantities. The reaction was found to fit a first order rate law and the mechanism suggested to explain this was

$$C_2H_5I \overset{1}{\rightleftharpoons} C_2H_4 + HI \text{ (slow)}$$

$$C_2H_5I + HI \longrightarrow C_2H_6 + I_2 \text{ (fast)}$$

The rate determining step is the slow elimination of HI. The rate constant for the elimination could be expressed:

$$\log k_1 = 13.36 - 50{,}000/2{,}303RT$$

The steady state concentration of HI was assumed to be low and the overall rate constant for the removal of ethyl iodide was therefore equal to $2k_1$. The interpretation of the data is complicated by the existence of an alternative mechanism:

$$C_2H_5I + I \overset{1}{\underset{2}{\rightleftharpoons}} C_2H_5 + I_2 \text{ (fast)}$$

$$C_2H_5 + I \xrightarrow[1']{} C_2H_4 + HI \text{ (rate determining)}$$

The rate law for this mechanism may be written:

$$-\frac{d(EtI)}{dt} = \frac{2K_{I_2}K_{12}k_1'}{k}(EtI)$$

Benson and Bose assigned E_1 = 1 kcal mole^{-1} and calculated values for k . The values obtained for E and A were too high compared with experimental results/

/results for the reaction to proceed entirely by this path. However the calculations indicated that the atomic mecnahism could account for 50% of the reaction at 292°C.

Guercione and Wijnen[100] studied the relative importance of recombination to disproportionation of I atoms and ethyl radicals by photolysis of diethyl ketone/methyl iodide mixtures. Their result was $k_{(disp.)}/k_{(recomb.)} = 0.33$.

Isopropyl Iodide

Four studies[88-91] have been made of the decomposition of isopropyl iodide. The overall chemical reaction was determined by Glass and Hinshelwood[88] to be $2iC_3H_7I \longrightarrow C_3H_8 + C_3H_6 + I_2$. Jones and Ogg[89] found the rate law $-\frac{d(iC_3H_7I)}{dt} = k(iC_3H_7I)$ held in the region 292° - 336°C with $k = 10^{13.20} \times 10^{-42,900/2.303RT}\ sec^{-1}$. Holmes and Maccoll[90] confirmed the above rate law in the temperature range 285° - 357°C but reported $k = 10^{14.40} \times 10^{-48,200/2.303RT}\ sec^{-1}$. Below 285°C they reported the rate law

$$\frac{d(I_2)}{dt} = k^1(iC_3H_7I)(I_2)^{\frac{1}{2}}$$

Benson and Teranishi[91] have studied the reaction over the temperature range 270° - 300°C and found no evidence for the I atom catalysis reported by Holmes. Benson and Teranishi assumed the rate determining step to be the elimination of HI and found the rate constant could be expressed $k = 10^{12.96}10^{-43,500/2.303RT}\ sec^{-1}$. Benson's values for k are 40% below those of Jones while Holmes' results are 20% below Benson's at 257°C and 40% at 290°C. Allowing for systematic experimental error Benson reduces the discrepancy between his and Jones' results to 20% and suggests this could be due to a temperature discrepancy between the laboratories of 2.5°C. It should be noted that Holmes and Maccoll were the only workers to use a vessel treated to prevent surface reaction and they have obtained the lowest rate.

n Propyl Iodide

Jones/

/Jones and Ogg[89] examined the decomposition of nPrI and found the overall reaction to be;

$$2C_3H_7I = C_3H_8 + C_3H_6 + I_2$$

and the rate law - $\frac{d(C_3H_7I)}{dt} = k(C_3H_7I)(I_2)^{\frac{1}{2}}$ to hold for the reaction.

Jones assumed that the rate determining step was the breaking of the R-I bond. Benson[87] points out that the kinetics cannot be explained this way and suggests as the rate determining step $I + nC_3H_7I \longrightarrow C_3H_6 + HI + I$. This is then followed by $nC_3H_7I + HI \longrightarrow C_3H_8 + I_2$.

n-Butyl Iodide

The decomposition of n-Butyl iodide was found[89] to give results similar to those found with n-propyl iodide. The ratio of final to inital pressure was greater than the 1.5 which would be expected from $2C_4H_9I \longrightarrow C_4H_8 + nC_4H_{10} + I_2$ and this is probably accounted for by the secondary reactions

$$nC_4H_{10} + I_2 \rightleftharpoons C_4H_8 + 2HI$$

$$\text{Butene-1} + I_2 \rightleftharpoons \text{1,3 butadiene} + 2HI$$

sec.-Butyl Iodide

Two studies[90,92] have been made of the decomposition of sec-butyl iodide. The results indicate that both a unimolecular elimination and an iodine catalysed reaction contribute to the decomposition.

t-Butyl Iodide

The decomposition of tBuI[89] was found to be heterogeneous and the products obtained were isobutene and HI suggesting that the elimination is so rapid that the iodine catalysed reaction does not compete with it.

Isobutyl Iodide

The rate law for the decomposition of isobutyl iodide is the same as that for nPrI and its decomposition mechanism is probably the same.

Benson/

/Benson[86] in reviewing the pyrolysis of the iodides has classified them under two rate determining reactions:

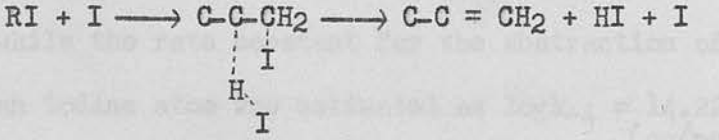
a) Unimolecular elimination of HI

EtI, iPrI and tBuI

b) I atom attack to give an olefine and HI.

nPrI, iBuI and nBuI.

For mechanism (b) the activation energy for the reaction has been found to be almost equal to the endothermicity. Benson has pointed out that the iodine atom reaction appears to become important when the atom can attack a secondary hydrogen atom. The concerted mechanism suggested by Benson is



3.7 Reaction of Iodides with HI

Ogg[93] measured the rate of the reaction of HI with methyliodide which he found reacted to give the parent hydrocarbon and iodine in equal quantities.

i.e. $RI + HI \longrightarrow RH + I_2$

Sullivan[94] and Benson[95] re-examined Ogg's data and found his deduction incorrect. Both workers found that the data was best explained by the following mechanism:

RI	$\longrightarrow R + I$	1
$I + RI$	$\longrightarrow R + I_2$	2
$R + I_2$	$\longrightarrow RI + I$	3
$R + HI$	$\longrightarrow RH + I$	4
$R + RI$	$\longrightarrow R\ I + RH$	5

Reactions 1 and 5 were not considered important by Benson and were not included. Sullivan included them in his treatment and showed that they were/

/were unimportant in all but the early stages where I acted as an initiation step. As Ogg gives only raw data for a small number of runs a further study of the reaction was made by Flowers and Benson[96] over the temperature range 260°- 310°C. In this work values for k_2, k_4 and k_3 were obtained along with an estimate of the value of the rate constant for the reverse of reaction 4. This was given as $\log k_{-4}$ (cc/mole.sec) $= 14.70 - 37,800/2,303RT$.

Ethyl Iodide + HI

Applying a method similar to that used by Benson and Flowers[96], Benson and Hartley[97] showed that the reaction of ethyl iodide with HI followed the same path as that for methyl iodide. Values for k_2, k_3 and k_4 were obtained while the rate constant for the abstraction of a hydrogen atom from ethane by an iodine atom was estimated as $\log k_{-4}$ (cc/mole-sec) $= 14.22 - 27,900/2,303RT$.

3.8 Addition of HI to Olefines

Ethylene

Benson and Bose[87] have studied the addition of HI to ethylene over the temperature range 289° to 331°C. They found the overall reaction to be:

$$C_2H_4 + 2HI \longrightarrow C_2H_6 + I_2$$

The pressure/time data fitted the second order rate law

$$-\frac{d(C_2H_4)}{dt} = k_2(C_2H_4)(HI)$$

and they explained the results by assuming the mechanism

$$C_2H_4 + HI \longrightarrow C_2H_5 \text{ (slow)}$$

$$C_2H_5I + HI \longrightarrow C_2H_6 + I_2 \text{ (fast)}.$$

As in the decomposition of ethyl iodide Benson points out the possibility of an alternative mechanism.

$$C_2H_4 + HI \underset{1}{\overset{2}{\rightleftharpoons}} C_2H_5 + I \text{ (slow)}$$

$$C_2H_5 + HI \longrightarrow C_2H_6 + I \text{ (fast)}$$

Benson/

/Benson makes rough estimates of the importance of this path by taking E_2 as 32.8 kcal mole^{-1} (i.e. $E_1 = 0$) and an A factor of the order of $10^{9.5}$. His results indicate that the atomic mechanism constitutes about 10% of the total reaction.

Propylene

The addition of HI to propylene has been studied[49] over the temperature range 230° to 270°C. The major product was found to be iPrI with less than 0.1% nPrI. At temperatures greater than 270°C the secondary production of C_3H_8 and I_2 was found to become important. The rate of addition was found to fit the second order rate law $\frac{d(iPrI)}{dt} = k(HI)(C_3H_6)$.

Isobutene

In the temperature range 201° to 245°C the reaction between HI and isobutene[52] was found to give as products isobutane and iodine. As in the case of propylene the rate law was second order mixed, i.e.

$$-\frac{d(ibutene)}{dt} = k(ibutene)(HI).$$

Butene-2

Benson and Nangia[98] found that HI reacted with butene-2 between the temperatures 292° and 333°C to give normal butane and iodine. The reaction products were explained by the mechanism

$$HI + \text{butene-2} \underset{2}{\overset{1}{\rightleftharpoons}} \text{sec } C_4H_9I \text{ (slow)}$$

$$\text{Sec } C_4H_9I + HI \longrightarrow nC_4H_{10} + I_2 \text{ (fast)}$$

Reaction 1 was found to have two paths:

a) direct molar addition and b) an iodine catalysed path. Study of this system is complicated by the iodine catalysed isomerisation reactions discussed/

/discussed previously[61-65].

Vinyl Chloride

Benson and Bose[52] attempted to study the addition of HI to vinyl chloride on the assumption that the mechanism would be similar to the other HI additions to olefines. They found, as well as the expected ethyl chloride and iodine, ethane, HCl and small amounts of ethylene. They point out that though the equilibrium $EtCl \rightleftharpoons C_2H_4 + HCl$ favours dissociation its rate is negligibly slow at 300°C, while they were working in the range 252 to 293°C. They conclude that by analogy with the iodine catalysed decomposition of nC_3H_7I[89] a similar reaction must occur with ethyl chloride.

$$I + EtCl \longrightarrow \begin{pmatrix} H_2C-CH_2 \\ H-Cl\cdots I \end{pmatrix} \longrightarrow C_2H_4 + HCl + I$$

Benson and Bose[99] have reviewed the data for four centre reactions using the iodide decompositions and addition of HI to olefines. The equivalent reactions of the chlorides and bromides have proved difficult to study due to the interference of chain reactions and surface effects and they have adjusted the data for these reactions so that it comes into line with the iodide results. They point out that the relative rates of elimination ($k(HI) > k(HBr) > k(HCl)$) can be explained on the basis of bond strength. The directional effect of an α methyl group (cf. addition of HI to C_3H_6 gives 99.9% iPrI) may be explained by assuming a highly polarised transition state. Evidence which supports this are the large dipole moments of the alkyl iodides compared with those of HI and the olefines.

CHAPTER II

AIM OF THE RESEARCH

If it is assumed that chain termination is by recombination of halogen atoms it is possible to describe the halogination of alkanes by reactions 1 to 6[28].

$M + X_2$	$\longrightarrow$	$2X + M$	1
$X + RH$	$\longrightarrow$	$R + HX$	2
$R + X_2$	$\longrightarrow$	$RX + X$	3
$R + HX$	$\longrightarrow$	$RH + X$	4
$X + RX$	$\longrightarrow$	$R + X_2$	5
$X + X + M$	$\longrightarrow$	$X_2 + M$	6

Here RH represents the alkane, X the halogen atom and M represents a third body. Reactions 4 and 5 inhibit the overall reaction but, owing to their endothermicity, have little influence on fluorination or chlorination studies except in the case of the chlorination of methane where $\frac{k_4}{k_3}$ has been found equal to 0.1. With bromine reaction 4 is generally exothermic but has been found relatively unimportant in comparison with 3. Reaction 4 is exothermic for all hydrocarbons with iodine atoms and as reaction 5 is less endothermic than 2 the equilibrium, $I_2 + RH \rightleftharpoons RI + HI$, is strongly in favour of hydrocarbon and iodine.

Owing to the rate of iodine atom recombination being very much faster than reaction 2[70-80] it is reasonable to assume that termination is entirely by reaction 6. This of course is not necessarily true for similar reactions of fluorine, chlorine and bromine.

A further complexity found with iodination of hydrocarbons is the instability/

/instability of the iodides at the temperatures required to obtain reasonable iodination reaction rates. The overall decomposition of the iodides may be expressed[86];

$$2RI \longrightarrow A + RH + I_2,$$

where A is an olefine. Detailed consideration of the mechanism shows that the initial step in the decomposition results in the production of an olefine and HI and then further reaction between iodide and HI, via reactions 4 and 5, result in the formation of parent hydrocarbon and iodine.

The object of the present study was to obtain values for the rate constant of reaction 2 with a number of hydrocarbons.

If reactions 7 and 8 are included in the mechanism:

$$RI \underset{8}{\overset{7}{\rightleftharpoons}} HI + A$$

the steady state method yields the rate law.

$$\frac{d(RI)}{dt} = \frac{(I)\ (k_2k_3(I_2)(RH) - k_4k_5K(A)(HI)^2)}{k_3(I_2) + k_4(HI)}$$

Here $K = \frac{k_7}{k_8} = \frac{(RI)eq.}{(A)eq.(HI)eq.}$

Stoichiometry gives (HI) = (RI) + 2(A) and if it is assumed that the iodide decomposition is almost complete, HI $\sim$ 2A, and by substitution in the above rate equation the following relationship is obtained.

$$\frac{d(A)}{dt} = \frac{(I)(k_2k_3(I_2)RH) - 4k_4k_5K(A)^3)}{k_3(I_2) + 2k_4(A)}$$

If $n = -\frac{2k_4(A)}{k_3(I_2)}$ and < 1, use of the expansion $\frac{1}{1-n} = 1 + n + n^2 + n^3$---- allows the rate law to be written in the form

$$\frac{d(A)}{dt} = k_2(RH)(I)\left\{1 - \frac{2k_4(A)}{(I_2)k_3} + \frac{4k_4^2(A)^2}{k_3^2(I_2)^2} + \text{----}\right\} - \frac{4k_4k_5K(A)^3}{k_3(I_2) + 2k_4(A)}$$

It/

/It can readily be observed that when (A) is very small in comparison with (RH) the reaction rate can be expressed, without serious error, as

$$\frac{d(A + RI)}{dt} = k_2(RH)(I)$$

As iodine atoms are in equilibrium with iodine molecules[24] the above expression becomes $\frac{d(A + RI)}{dt} = k_2 K_{I_2}^{\frac{1}{2}}(RH)(I_2)^{\frac{1}{2}}$ where $K_{I_2}^{\frac{1}{2}} = \frac{(I)eq.}{(I_2)eq.}$

By measuring the rate of product formation in the early stages of the reaction, using a sensitive analytical technique such as gas chromatography and plotting their concentration against the function $(RH)(I_2)^{\frac{1}{2}}t$, (t = time), a straight line plot should be obtained with slope equal to $k_2 K_{I_2}^{\frac{1}{2}}$ and, as K_{I_2} may be calculated from well established thermodynamic data, values for k_2 may be obtained.

The advantage which iodination studies have over the same reactions of the other halogens is the specific nature of the iodine atom attack on the hydrocarbon. Owing to the high activation energies of these reactions it is possible to select a temperature range over which the attack of the iodine atom will be almost entirely on the hydrogen atom with the weakest C-H bond. It is then possible to estimate, using the measured activation energy and an estimate of that for the back reaction, the strength of the C-H bond.

It was initially intended to study the overall equilibrium $RH + I_2 \rightleftharpoons A + 2HI$ but the detection of secondary products in reactions which were allowed to proceed towards equilibrium indicated that the systems were more complex than expected. A number of secondary products have been identified and mechanisms for their formation suggested.

CHAPTER III

EXPERIMENTAL

1. Materials

1.1 Reactants:-

Iodine was supplied by B.D.H. and was of "Analar" grade. It was further purified by a method which will be described in the section on procedure.

Isobutane (British Petroleum Cylinder) was collected at - 193°C (liquid nitrogen) and dried over P_2O_5. The gas was distilled several times from - 80°C (powdered solid CO_2 in acetone) to - 193°C. Impurities detected by gas chromatographic analysis indicated that n-butane (0.4%) and propane (0.04%) were present as impurities.

Propane

The initial work with propane was carried out using a sample from an I.C.I. cylinder. The raw material was found to contain 1.6% isobutane, 0.32% propylene and 0.2% ethane. Use of a preparative scale gas chromatography column, (Al_2O_3 deactivated with 5% dinonyl phthalate), reduced the isobutane to 0.2%. In calculating results obtained with this material allowance was made for the 0.32% propylene. The bulk of the kinetic studies were carried out with Matheson Research Grade propane which after treatment identical to that given to the isobutane contained 0.1% isobutane.

Ethane (B.O.C. cylinder) was passed through a series of three gas wash bottles containing fuming sulphuric acid followed by a 2 foot column of activated carbon saturated with bromine. The gas was then passed through a trap at - 80°C before being collected at - 193°C. The ethane was dried over P_2O_5 and submitted to a number of trap to trap distillations from

-80°C/

/ -80°C to - 193°C. After this treatment the ethane was found to contain 0.4% propane.

n-Butane was supplied by B.H.C. and contained 0.4% i butane. To remove the impurity the gas was brominated for 2 hours in a glass bulb illuminated by a tungsten lamp. The gas was distilled a number of times from - 80°C to - 193°C and dried over P_2O_5. The n-butane finally contained 0.1% i-butane.

1.2 Materials for Calibration of the Thermocouple:-

Cadmium, Tin and Zinc were high purity "Analar" samples (B.D.H.). Maximum percentage impurities were Cadmium 0.03%, Tin 0.03% and Zinc 0.01%.

1.3 Analytical Materials:-

Auramine bis(p-dimethyl amino phenyl) methyleneimine

Technical grade auramine (B.D.H.), used to remove HI from the reaction products, was found to be unsuitable as a gas filter as it tended to form non-porous plugs. When it was mixed with powdered firebrick (60-80 mesh) in the ratio 2/3 by volumne a satisfactory material was obtained.

Alkyl Iodides were B.D.H. reagents. They were shaken with mercury to remove iodine and dried over P_2O_5. They were distilled from 0°C to -80°C and stored at 0°C.

Benzene, p-xylene and o-xylene were B.D.H. reagents and were used without purification.

Hydrogen (B.O.C. cylinder) was dried before use by passing through a tube packed with activated molecular seive (Linde 5A Grade).

Compressed Air (B.O.C. cylinder) was passed through a tube packed with glass wool coated with Apiezon grease, which acted as a dust filter, and then dried in the same manner as the hydrogen.

Chromatography/

/Chromatography Column Packings:-

Alumina was supplied by P. Spence & Sons, Widnes , Lancashire.

Firebrick was fosalsil No. 6 powder from Moler Products, Colchester.

Celite was G. Cel plain supplied by Gas Chromatography Ltd., Maidenhead.

Stationary Phase Materials:-

Dinonyl phthalate and diethyl adipate were B.D.H. reagents.

Tween 60 was supplied by L. Light and Co.

2. Apparatus

The experimental apparatus will be described in two sections 1) kinetic apparatus 2) analytical apparatus.

2.1 Kinetic Apparatus

The kinetic apparatus (figure 2) was constructed of pyrex glass and was evacuated by means of a mercury diffusion pump, backed by a rotary oil pump, to a vacuum of 10^{-5} mm. Hg measured on a simple mercury vacuostat. The apparatus is best described in three sections all of which were evacuated via the same vacuum line.

a. Section at 120°C.

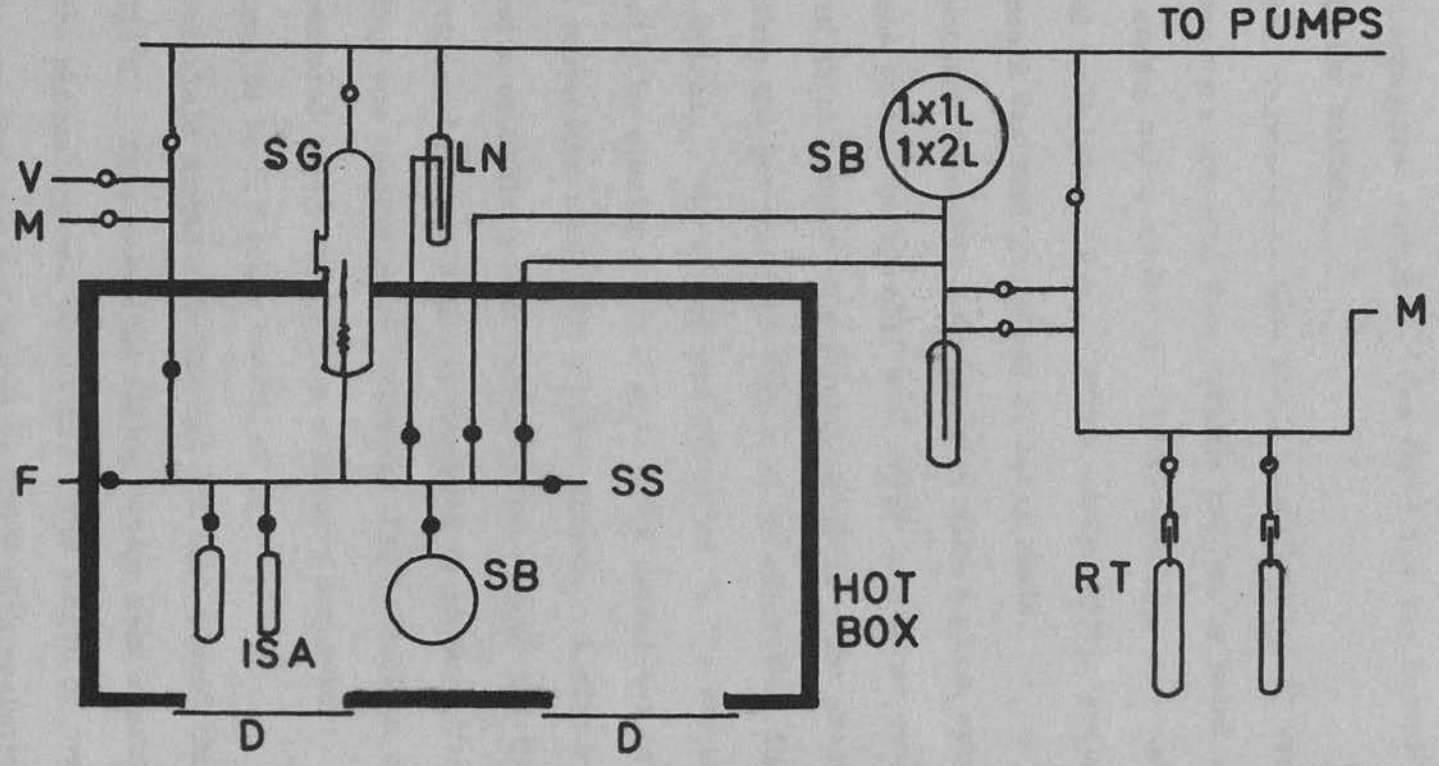
b. Section at room temperature.

c. Furnace section.

a. Section at 120°C

This section was used for the storage and handling of iodine in the vapour phase (vapour pressure of I_2 at 120°C = 110 mm.). It was enclosed in a rectangular, double walled, box constructed of wood asbestos. The external dimensions of the box were 96 cms. x 41 cms. x 32 cms. The wall thickness was 4.5 cms and the space between the two layers of asbestos sheeting was packed with mineral wool. The base of the box was fitted with two doors which allowed cold baths to be applied to the iodine storage bulbs and "u" tubes of the/

FIGURE-2 KINETIC APPARATUS



V = VACUOSTAT
M = MANOMETER
F = TO FURNACE SECTION
ISA = IODINE STORAGE AMPOULES
SB = STORAGE BULBS
SS = TO SAMPLING SYSTEM
SG = SPIRAL GAUGE
LN = LIQUID NITROGEN TRAP
D = DOOR
o GLASS STOPCOCK
• HONE VALVE
RT = REMOVABLE TRAP

/the analytical sampling system. One side of the box was fitted with windows to allow observation of the apparatus and this side could be removed when the apparatus required repairs. The "hot" box was heated by a silica covered electric bar heater.

Metal valves (F.J. Hone Ltd., London) (fig. 3) were used in this section and these were operated from outside the box by metal rod extensions screwed to the normal valve controls. Valve seatings were made from a filled teflon supplied by Polypenco Ltd., (Welwyn Garden City). "Araldite", (C.I.B.A., Cambridge), epoxy resin was used for glass to metal seals.

Reactant pressures were measured with a glass spiral gauge (figure 4). The glass spiral was mounted vertically in a glass canopy containing liquid paraffin which reduced vibrational effects. The greater part of the canopy was within the hot box (see figure 2) in order that iodine would not condense in the spiral. The canopy was connected to the vacuum line and was degassed frequently by opening a glass tap. The spiral was held in position by a torque suspension made with a nylon thread. A mirror was fixed to this suspension opposite a flat window in the canopy and this was used along with a conventional lamp and scale arrangement to measure the movement of the gauge. The gauge was calibrated by measuring the deflection obtained from pressures of air measured simultaneously on a mercury manometer. The gauge sensitivity was found to be 3.7 scale cms/cm of Hg.

Materials pumped from the hot box were passed through a removeable trap at - 193°C. This prevented iodine vapour from reacting with mercury vapour from the manometers and vacuostat. The length of pyrex tubing between the hot box and the trap was heated to 120°C with resistance tape.

Iodine was stored in two glass traps (50 c.c. and 100 c.c.) and the iodine was exhaustively degassed prior to each run.

b. Section/

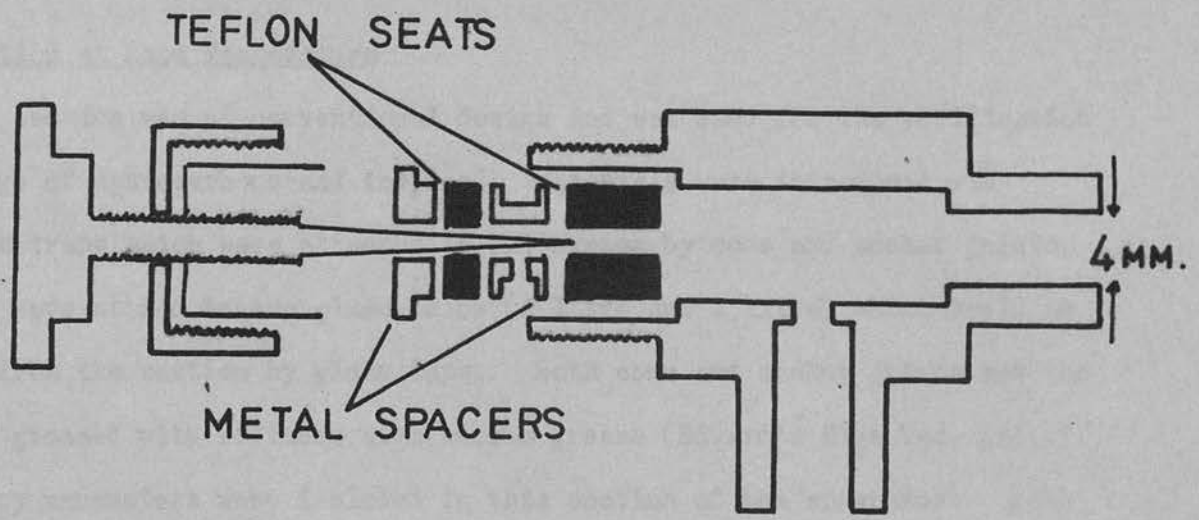


FIGURE-3 HONE VALVE

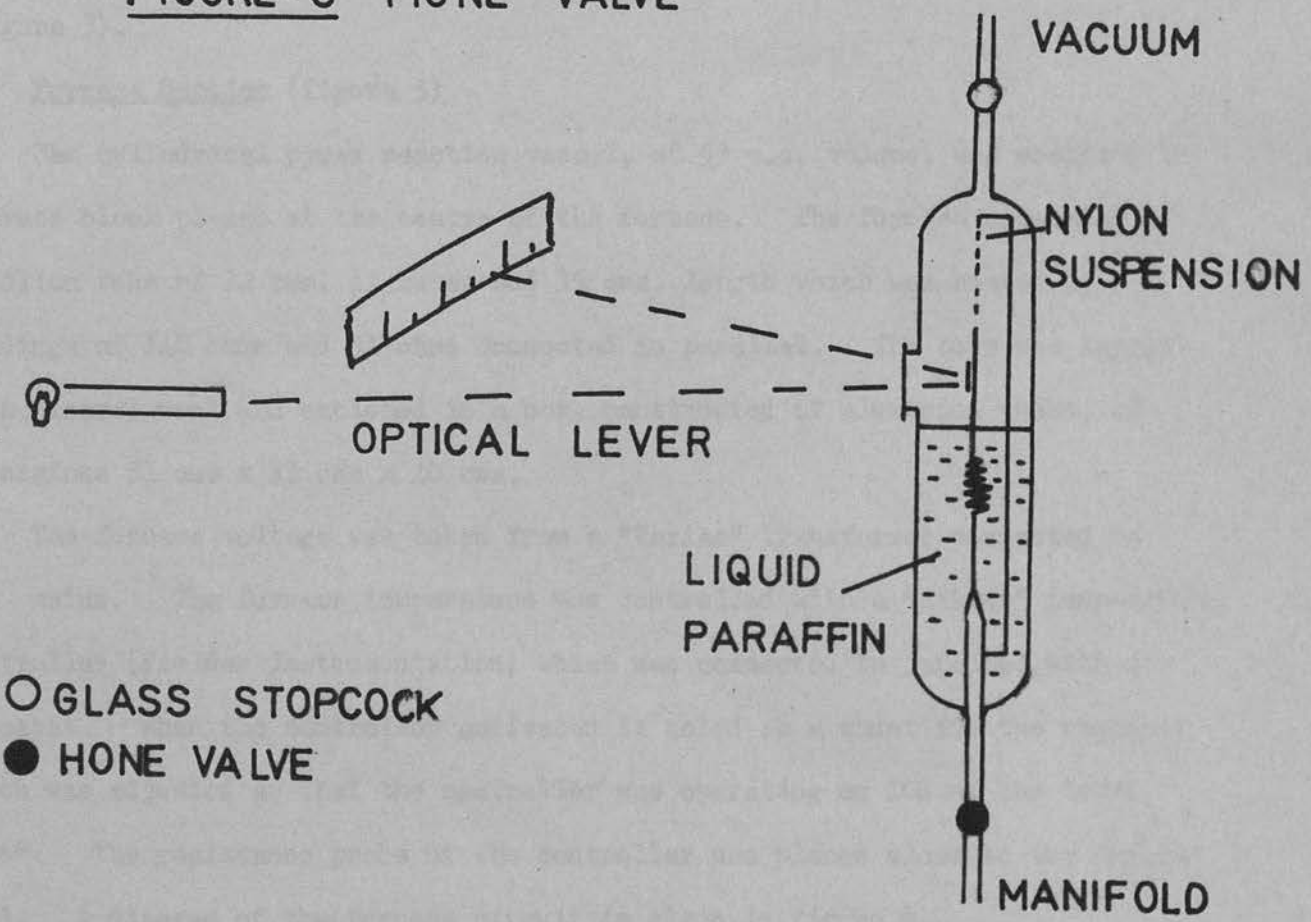


FIGURE-4 SPIRAL GAUGE

b. /Section at Room Temperature

This section was of conventional design and was used for the purification and storage of hydrocarbons and iodides. Materials were introduced via removeable traps which were attached to the system by cone and socket joints. Materials were stored in two glass bulbs (2 litre and 1 litre) which could be isolated from the section by glass taps. Both cone and socket joints and the taps were greased with silicone high vacuum grease (Edward's High Vac. Ltd.,). Two mercury manometers were included in this section of the apparatus. Both the storage bulbs and one of the mercury manometers were connected to the section of apparatus at 120°C via metal valves. (F.J. Hone Ltd., London) (figure 3).

c. Furnace Section (figure 5)

The cylindrical pyrex reaction vessel, of 53 c.c. volume, was enclosed in a brass block placed at the centre of the furnace. The furnace consisted of a silica tube of 12 cms. diameter and 35 cms. length which was heated by windings of 140 ohmn and 51 ohmn connected in parallel. The tube was lagged with mineral wool and enclosed in a box, constructed of aluminium sheet, of dimensions 31 cms x 31 cms x 40 cms.

The furnace voltage was taken from a "Variac" transformer connected to the mains. The furnace temperature was controlled with a "Bikini" temperature controller (Fielden Instrumentation) which was connected in parallel with a rheostat. When the controller activated it acted as a shunt for the rheostat which was adjusted so that the controller was operating on 10% of the total power. The resistance probe of the controller was placed close to the furnace wall. A diagram of the furnace circuit is given in figure 6.

The brass block was cylindrical in shape and of 20 cms length and 9 cms diameter./

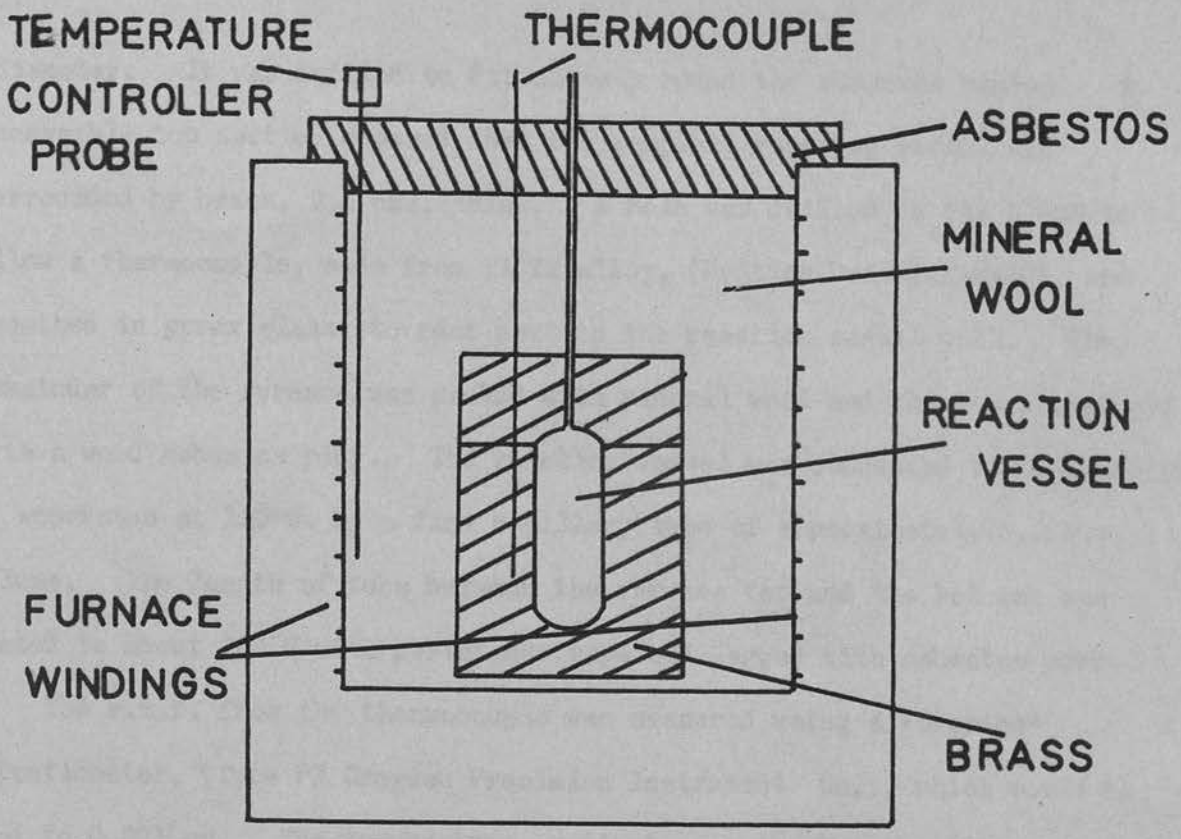


FIGURE-5 FURNACE SECTION

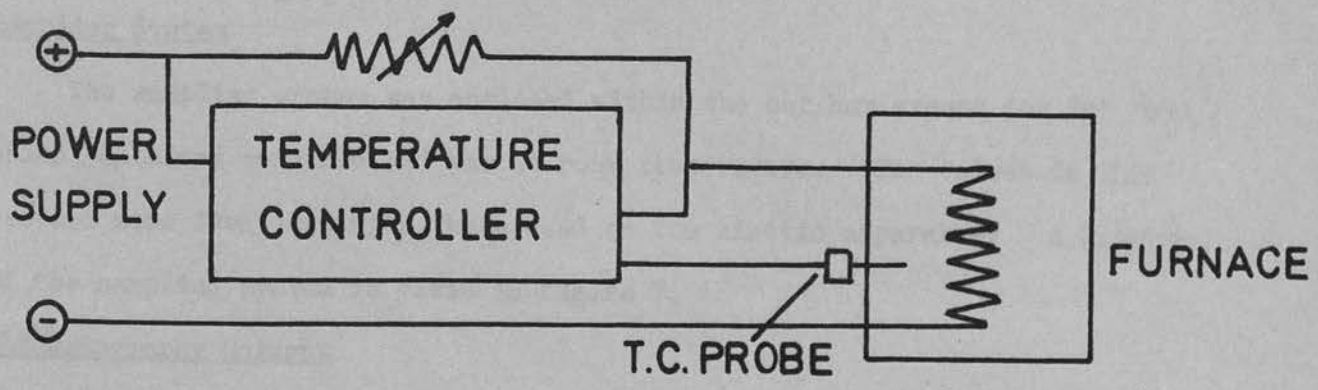


FIGURE-6 FURNACE CIRCUIT

/diameter. It was drilled to fit closely round the reaction vessel. A removeable top section ensured that the complete reaction vessel was surrounded by brass, 2.5 cms. thick. A hole was drilled in the block to allow a thermocouple, made from T1/T2 alloy, (British Driver-Harris), and sheathed in pyrex glass, to rest next to the reaction vessel wall. The remainder of the furnace was packed with mineral wool and the top closed off with a wood asbestos plug. The reaction vessel was connected to the section of apparatus at 120°C. by a fine capillary tube of approximately 0.2 c.c. volume. The length of tube between the furnace top and the hot box was heated to about 250°C with resistance tape and lagged with asbestos cord.

The e.m.f. from the thermocouple was measured using a "Cropico" potentiometer, (Type P3 Croydon Precision Instrument Co.), which could be read to 0.001 mv. The temperature gradient over the length of the brass block was negligible at this accuracy.

Tests for surface reaction were carried out in a vessel of dimensions identical to that described above but packed with fine glass tubing, (1 mm.diam), so that the surface to volume ratio was increased from 1.6 $cm.^{-1}$ to 20 $cm.^{-1}$.

2.2 Analytical Apparatus

Sampling System

The sampling system was enclosed within the hot box except for "u" tube A which contained auramine and was at room temperature. The valves in this section were identical with those used on the kinetic apparatus. A diagram of the sampling system is given in figure 7.

Chromatography Columns

Table (III.1) describes the columns along with the retention times of reactants and products.

In/

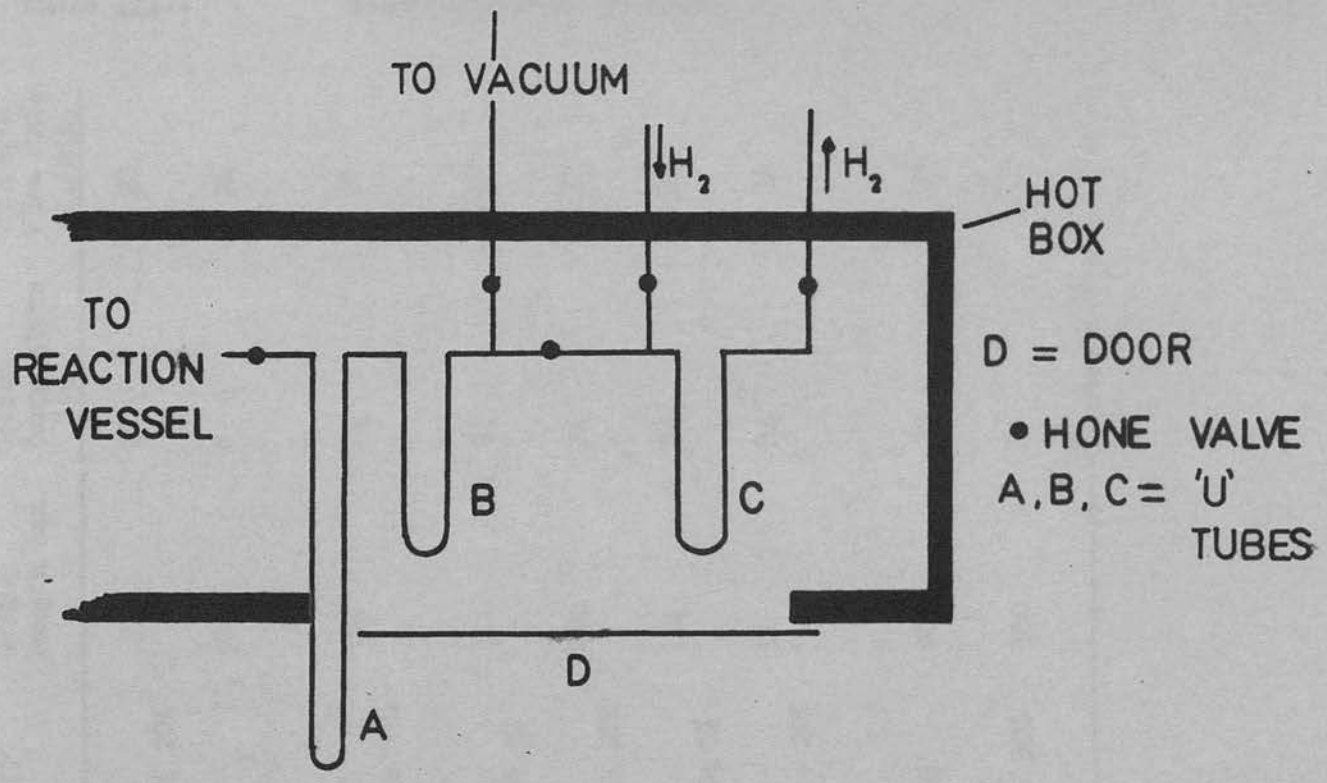


FIGURE - 7 SAMPLING SYSTEM

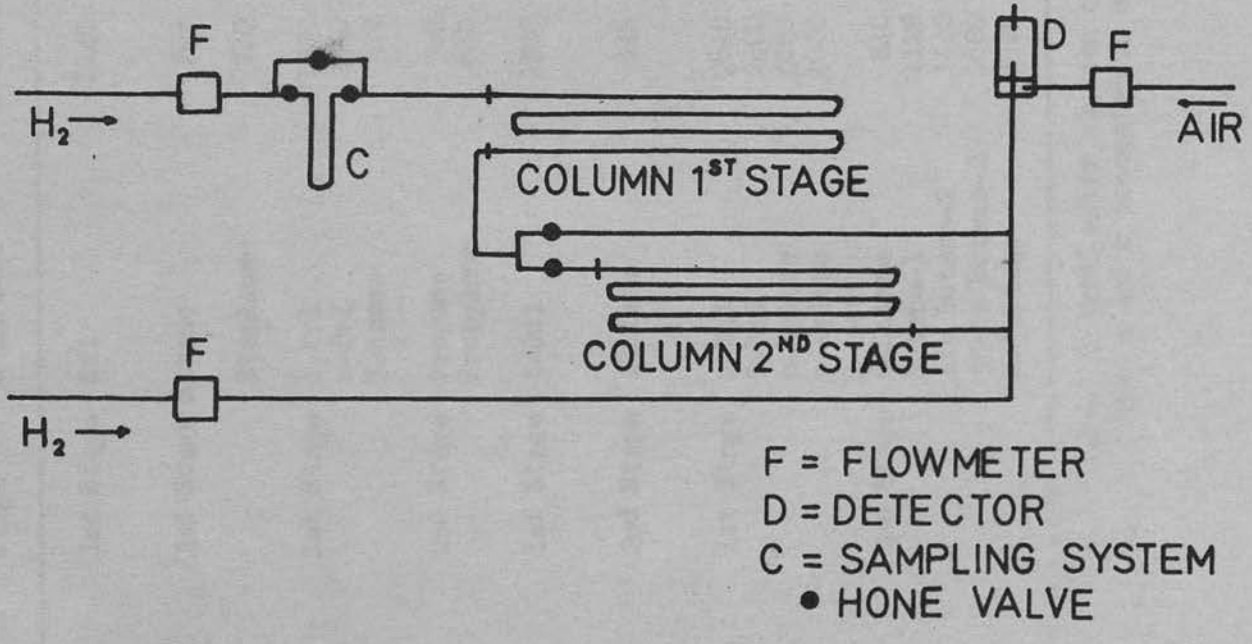


FIGURE - 8 CHROMATOGRAPHY APPARATUS

Table III.1 CHROMATOGRAPHY COLUMNS

Column Number	Column Stage	Substances Separated	Retention Time secs.	Column Packing	Stationary Phase	Column Length cms.	Column Temperature °C	Hydrogen Flow Rate ml./min.
1.	1st Stage	EtI	1140	Celite (60-100)	Dinonyl Phthalate 20%	51	23	20
	2nd Stage	Ethane	509	Activated Al_2O_3 (60-90)	-	570	0	20
		Ethylene	710					
2.	1st Stage	i-PrI	1200	Celite (60-100)	Dinonyl Phthalate 20%	61	24	29
		n-PrI	2460					
		Benzene	912					
	2nd Stage	Propane	360	Al_2O_3 (60-90)	Dinonyl Phthalate 5%	224	24	29
		Propylene	660					
3.	1st Stage	t-BuI	2880	Celite (60-100)	Dinonyl Phthalate 20%	244	34	34
	2nd Stage	iButane	648	Al_2O_3 (60-90)	Dinonyl Phthalate 5%	124	34	34
4.	1st Stage	n-BuI	2640	Celite (60-100)	Dinonyl Phthalate 20%	51	34 [1]	16
		i-BuI	2400					
		o-Xylene	4080					
		p-Xylene	4000					
	2nd Stage	n-Butane	840	a) [2] Celite (60-100)	Tween 20%	200	30	16
		Butene-1	1128					
		cis Butene-2	1440	b) Firebrick (60-80)	Diethyl adipate 30%	300	0	
		trans Butene-2	1680					
		Butadiene	1920					

1. Raised to 60°C after elution of butadiene.
2. Columns a and b connected in series.

/In order to measure both hydrocarbons and iodides in a relatively short time a two stage column was used (figure 8). The high boiling iodides were retained on the first stage while the low boiling hydrocarbons were separated on the second stage. The length and temperature of the 1st stage was adjusted so that the high boiling material was eluted from it just after the final peak had been eluted from the second stage. The gas flow from the 1st column could be fed directly to the detector and the flow stopped from passing to the second column by means of a Y junction fitted with two Hone valves. In order to retain the same flow rate when the resistance of the second stage had been removed a needle valve (Griffin & George) was placed between the detector and the end of the first column and adjusted to have a resistance to flow identical with that of the 2nd stage of the column.

All columns were of pyrex glass (4 mm. diam.), glass leads of pyrex capillary tubing (0.5 mm. diameter) and rubber tubing was used for glass to glass joins. The glass to metal valve connections were made by tightening a nut on a polythene "o" ring. Columns were constructed from a series of "u" shaped lengths and were thermostatted in a cylindrical glass jacket heated by resistance tape or in a lagged glass tube packed with ice.

Gas flows were controlled by needle valves (Edwards High Vacuum) and measured on capillary meters,[101] of conventional design, which had been calibrated against a bubble flow meter.[101]

Detector (figure 9)

A hydrogen flame ionisation detector was made from brass following a design given by Desty[102]. The detector was supplied with compressed air (800 ml./min.) and a subsidary hydrogen flow of 20 ml./min. which kept the detector flame alight during sample injection. The detector jet was maintained at 270v by three 90 volt dry batteries connected in series. The detector/

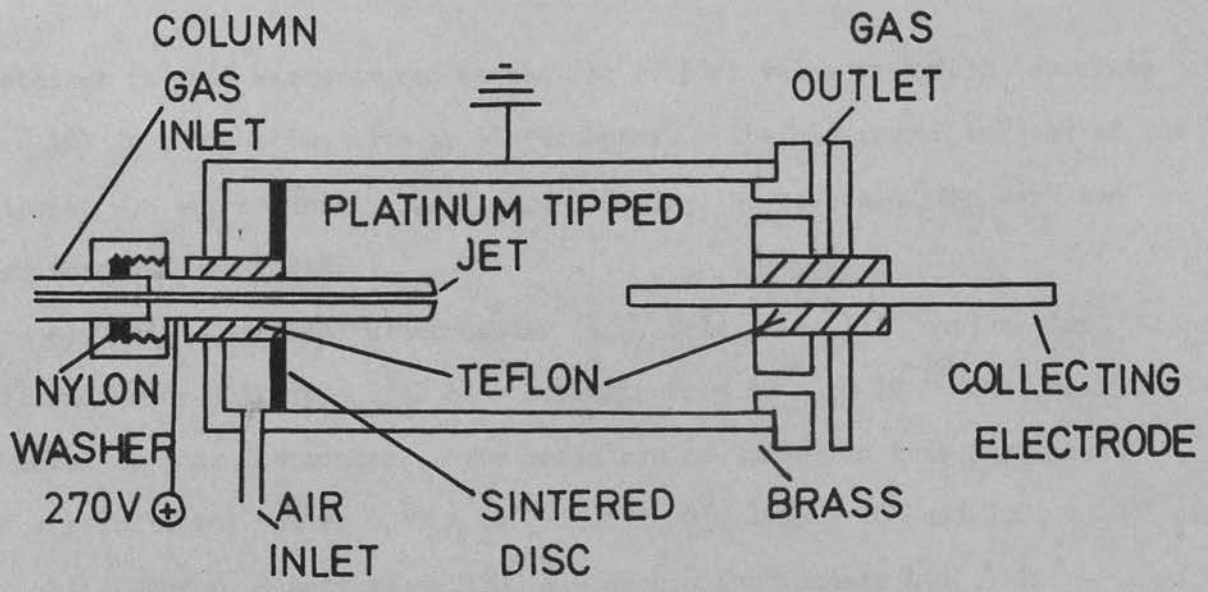


FIGURE-9a FLAME IONISATION DETECTOR

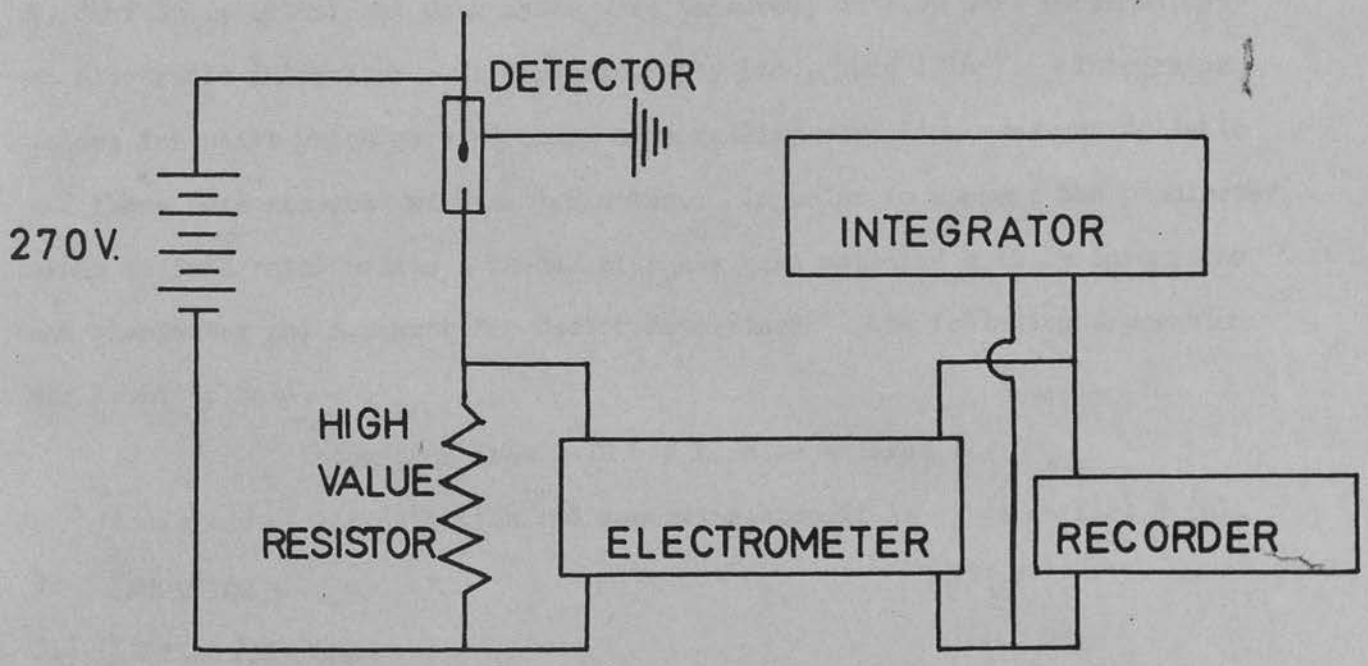


FIGURE-9b DETECTOR CIRCUIT

/detector current was measured by the use of high value resistors (accurate to $\pm$ 1%) in conjunction with an electrometer. The background current of the detector was approximately 10^{-12} amp. During the course of the work two electrometers were used.

a) Vibrating Reed Electrometer (E.K. Cole, Ltd.,) in conjunction with Indicator Unit Type 1341 A. Currents from 10^{-6} to 10^{-12} amp. could be measured on this instrument. The resistors contained in this instrument had the following values 0.97×10^{7}, 1.16×10^{8}, 1.05×10^{9} and 1.04×10^{10} ohmn.

b) Vibrom Electrometer 33B (Electronic Instruments Ltd.,) in conjunction with Shunt Unit A49A. This unit contained resistors with the following values 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8}, 10^{-9}, 10^{-10}, 10^{-11} ohmn. Currents from 10^{-5} to 10^{-13} amp. could be measured on this instrument.

Recording

The electrometer output was recorded on almv. recorder (Mark 3, G. Kent Ltd., Luton) and peak areas were measured, as they were recorded, by an electronic integrator (Gas Chromatography Ltd., Model 1E165). Integrator values for peaks which were recorded on a falling base line were not reliable and these were measured with a planimeter. In order to convert the planimeter areas to integrated values a number of peaks were measured both by integrator and planimeter and a conversion factor determined. The following expression was found to hold.

Integrator Area = 10.6 x Planimeter Area.

A diagram of the detection and recording circuit is given on fig. 9 (b).

3. Procedure

3.1 Kinetic Procedure

The apparatus, excepting storage bulbs, was first evacuated. Iodine vapour was then allowed to fill the reaction vessel and manifold at 120°C to

a/

/a pressure measured by the spiral gauge. The valve to the reaction vessel was then closed and the iodine remaining in the manifold frozen back into the storage ampoule which was then closed. The manifold was then pumped out and hydrocarbon measured into it from a storage bulb. The pressure of the hydrocarbon in the manifold was always greater than that of the iodine already in the reaction vessel. The valve to the reaction vessel was then opened and a stopwatch started. After 5 to 10 seconds the equilibrium pressure was reached and the valve to the reaction vessel closed. The equilibrium pressure was then read from the spiral gauge. The pressure of hydrocarbon in the reaction vessel was then calculated by subtracting the pressure of iodine in the reaction vessel from the equilibrium pressure. The hydrocarbon remaining in the manifold was pumped away. At the completion of the reaction the valve to the reaction vessel was opened and the reaction mixture frozen down in "u" tube B (figure 7). On opening the valve the time on the stopwatch was noted. The freezing down process required in the region of 10 to 15 seconds, using the return to zero of the spiral gauge as a measure of the condensation of the reaction mixture. To ensure that all the reactants and products had been collected the process was allowed to continue for five minutes with the reaction vessel being pumped out through "u" tube B for about one minute after this period. In passing from the reaction vessel to B the gases were filtered through auramine placed in tube A. This removed HI by adsorption and as this tube was at room temperature excess iodine also condensed here. The HI was removed at this point in order to prevent it recombining with unsaturated material in tube B. The extent to which the auramine had been saturated was indicated by the distinctive red colour obtained when HI reacts with the normally yellow auramine. The auramine was replaced when two thirds of its length had become red.

Tests were made to ensure that iodide decomposition did not occur on the/

/the auramine. This involved measuring the peak areas of iodide samples, of known pressure, measured in the manifold, some of which were not passed through the auramine. Iodide decomposition could also be checked for by testing for the presence of likely reaction products (i.e. olefines). No decomposition was detected except in the case of t-butyl iodide where the test was not reliable as tBuI was found to decompose in manifold, which was at 100°C during the tests.

After the sample had been collected in "u" tube B it was distilled into "u" tube C. This was carried out by surrounding tube B with an ice trap and "u" tube C with a Dewer vessel containing liquid nitrogen. The ice trap was used to prevent any iodine which had not condensed in A from reaching C. Test runs showed that 15 minutes was adequate to allow complete distillation of iodides and hydrocarbon. After the distillation process the valve between B and C was closed and the sample for analysis injected onto the chromatography columns by opening the taps to the hydrogen leads and surrounding C with a vessel containing boiling water.

3.2 Calibration of Thermocouple

The thermocouple used for measuring the temperature of the reaction vessel was calibrated using the freezing points of zinc, cadmium and tin as standards. Figure 10 gives a diagram of how the apparatus was assembled. The metal bath was first heated above the melting point of the metal and the thermocouple junction, sheathed in pyrex, inserted. The furnace supply was turned off and the thermocouple voltage plotted against time as the metal cooled. The e.m.f's were measured with the "Cropico" potentiometer. Two runs were carried out with each metal as this allowed the thermocouple junction to be placed at different levels in the metal bath in order to check the effect of conduction along the thermocouple leads. Change of junction position had negligible effect on the voltage measured.

The/

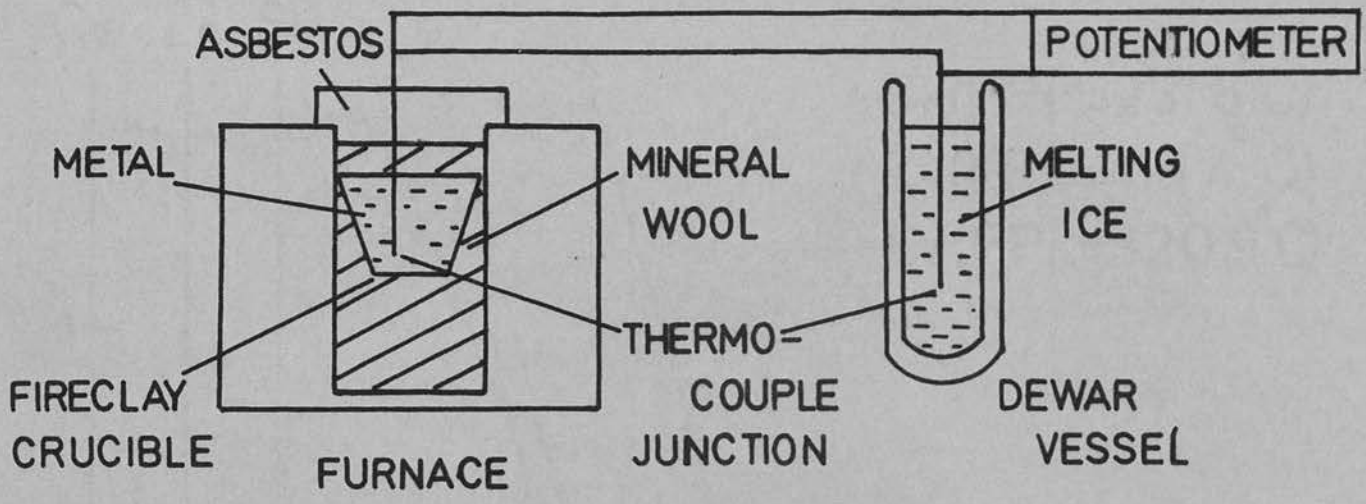


FIGURE-10 THERMOCOUPLE CALIBRATION APPARATUS

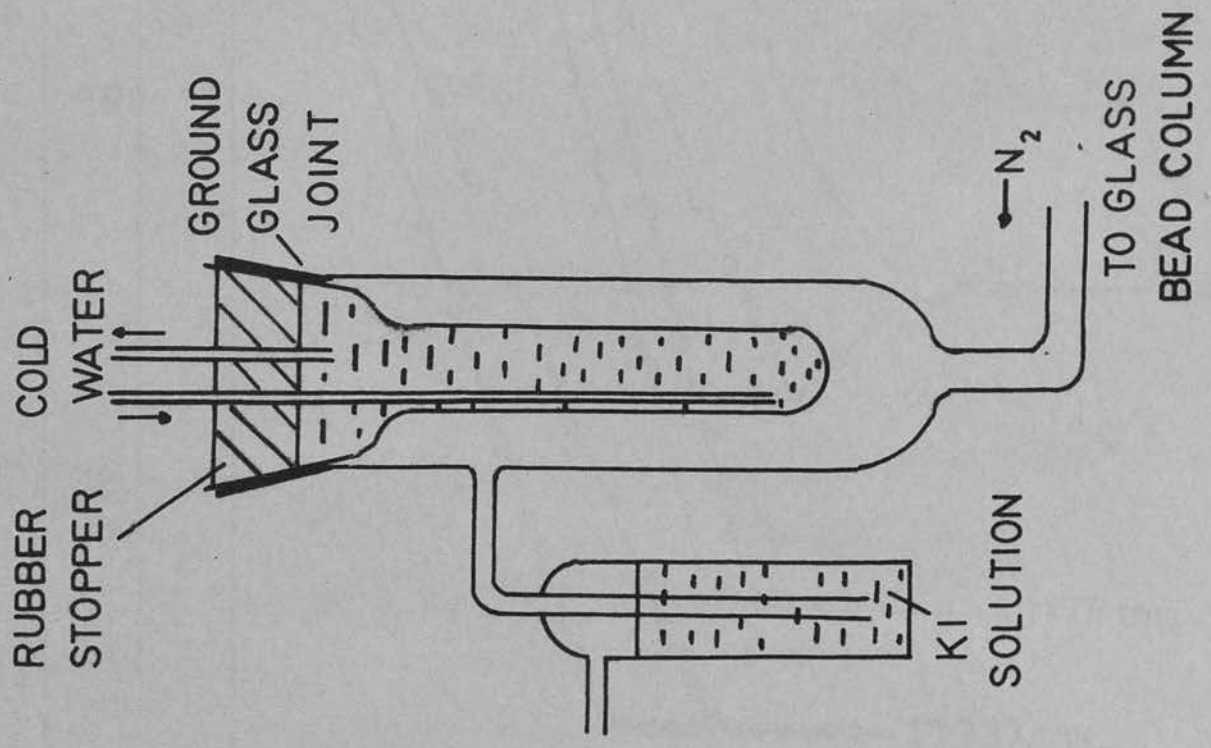


FIGURE-12 IODINE PURIFICATION APPARATUS

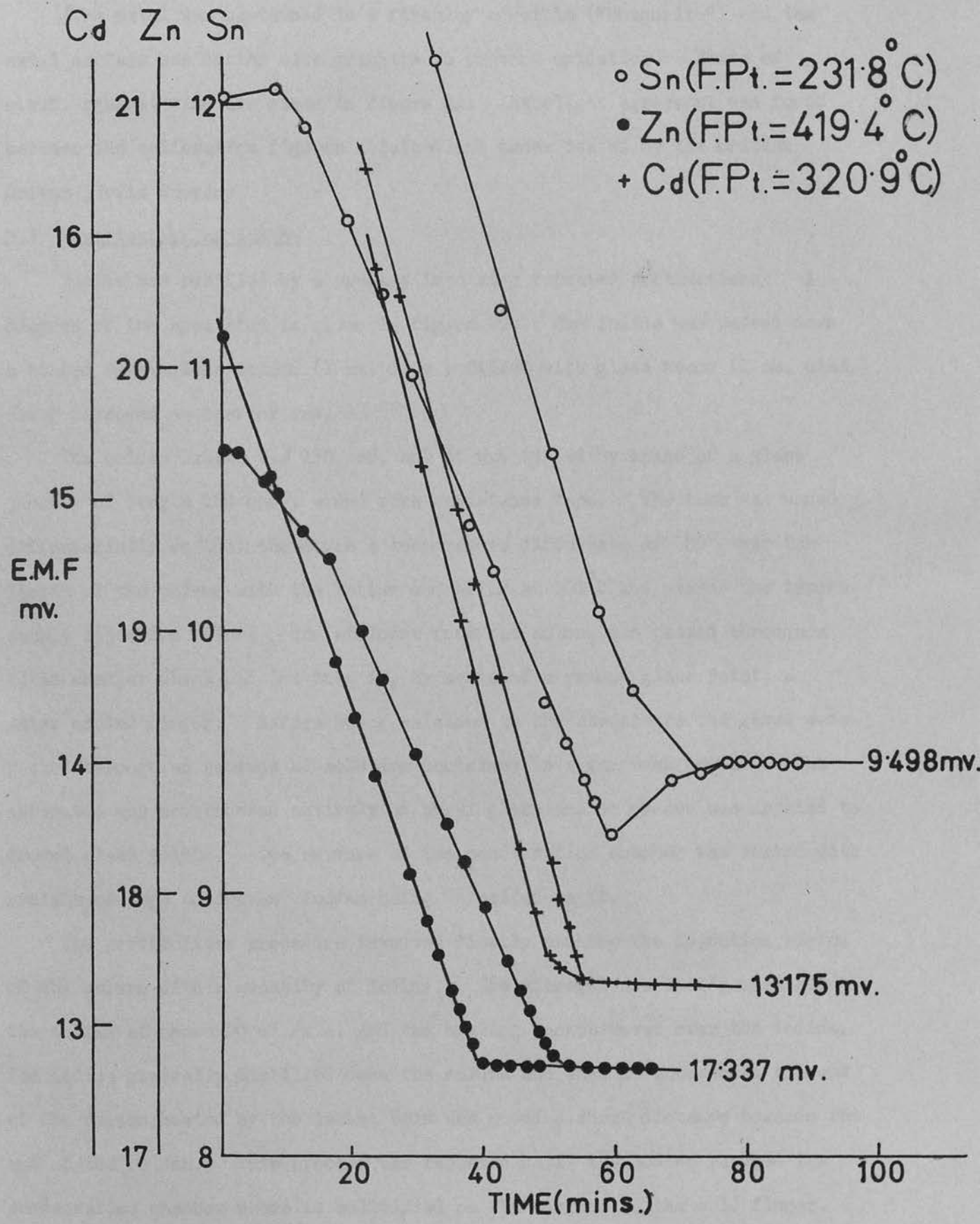


FIGURE-11 THERMOCOUPLE CALIBRATION DATA

/The metal was contained in a fireclay crucible ("Morganite") and the metal surface was dusted with graphite to prevent oxidation. Plots of e.m.f. against time are given in figure 11. Excellent agreement was found between the calibration figures obtained and those issued by the British Driver-Harris Company.

3.3 Purification of Iodine

Iodine was purified by a process involving repeated sublimations. A diagram of the apparatus is given in figure 12. The iodine was passed down a heated pyrex glass column (1 cm. diam.) filled with glass beads (1 mm. diam.) using nitrogen as carrier gas.

The column length was 130 cms. and it was heated by means of a glass jacket, of length 100 cms., wound with resistance tape. The tape was wound differentially so that there was a temperature difference of 100° over the length of the column with the hotter end being at 200°C and nearer the impure sample injection point. The effluent from the column was passed through a glass chamber which had let into it, by means of a ground glass joint, a water cooled finger. Before being released to the atmosphere the gases were passed through an aqueous KI solution contained in a gas wash bottle. The apparatus was constructed entirely of pyrex glass and no grease was applied to ground glass joints. The surface of the condensation chamber was heated with resistance tape to prevent iodine being deposited on it.

The purification procedure involved firstly packing the injection region of the column with a quantity of iodine. The nitrogen was then passed along the column at about 20 ml./min. and the heating jacket moved over the iodine. The iodine gradually distilled down the column and when it approached the end of the region heated by the jacket this was moved a short distance towards the end of the column. This process was repeated until the iodine reached the condensation chamber where it solidified on the surface of the cold finger.

The/

/The cold finger was then removed and the iodine transferred to a glass ampoule which was then attached to the kinetic system at a point within the hot box.

After a series of runs a white deposit was observed at the injection point and as this proved involatile when heated with a bunsen flame it was assumed to be an inorganic salt. When the iodine was initially heated a brown material was swept away by the nitrogen. Until this material had been carried through to the KI solution the cold finger was not put in place and the socket was closed with a stopper.

3.4 Preparation of Chromatography Columns

Column packings were prepared in the conventional manner[103]. The liquid phase was dissolved in a suitable low boiling solvent and this solution was mixed with the inert solid material opon which the liquid phase was to be deposited. The low boiling solvent was then taken off with a water pump and the remaining material packed into pyrex columns.

3.5 Treatment of Results Data

Sternberg and his co-workers[104] have shown that the response of a hydrogen flame detector is proportional to the number of carbon atoms in the molecule and that olefines and monohalides can be considered to have the same sensitivity as the parent hydrocarbon. They have also shown that the linearity of the detector is in excess of 10^7 fold. These results mean that in the present work all products could be considered to have a detector sensitivitydirectly proportional to their carbon number and that no correction was required for the considerable difference in concentration between the reactant hydrocarbon and products.

By adding the peak areas for reactant and product hydrocarbons, adjusted to the same sensitivity, an area equivalent to the total hydrocarbon initially in/

/in the reaction vessel was obtained. The concentration of the products could then be estimated from the % composition of the final reaction mixture calculated from peak areas.

CHAPTER IV

RESULTS

The experimental data is presented in tubular form (Tables IV.1 to IV.49) along with data for the function $(I_2)^{\frac{1}{2}}$ (RH)t, where t = time, which was used to determine the value of k_2, i.e. the abstraction rate constant. The values of k_2 were calculated by two methods. Firstly the data was plotted in the form Total Products against $(I_2)^{\frac{1}{2}}$ (RH)t and the "best" straight line drawn through the origin and the points. From the gradient the value of k_2 was calculated. Secondly the values of k_2 obtained by drawing lines through the origin and each point were averaged. The values of k_2 determined by the two different methods were always in excellent agreement. The analytical peak areas given for the products are not the raw experimental values but represent these corrected to the same sensitivity as that used to measure the reactant hydrocarbon. Appended to each table is information regarding the detector sensitivity used to measure the reactant hydrocarbon, whether the peak areas have been measured by planimeter or integrator and a reference to the appropriate figure where the data has been plotted graphically.

Tables IV 20, IV 33 and IV.49 tabulate the values found for k_2 and other data used to make the Arrhenius plots for C_2H_6, C_3H_8, and iC_4H_{10} respectively. The values of A and Eact. determined from these plots by the method of least squares are appended to these tables. Also included in the above tables are the values of K_{I_2}, the iodine dissociation equilibrium constant, used to calculate k_2. The values of K_{I_2} were calculated from the thermodynamic data given in Table V.1.

IV.1 The Reaction of Iodine with Ethane in the temperature range 290°C to 245°C

The following tables give the experimental data for the reaction of iodine with ethane. The tables are listed in order of increasing temperature and the runs are numbered in the order in which they were carried out. The ethylene peak areas were measured by planimeter and these values converted to integrator values. At the lower temperatures no ethylene was detected in the products.

Table IV.1

Iodine + Ethane 291.0°C (564.2°K)

Run	$(I_2)\times10^7$ moles cc^{-1}	$(C_2H_6)\times10^6$ moles cc^{-1}	Time(t) secs.	$F\times10^7$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $\times 10^9$ moles cc^{-1}
114	2.90	1.71	3480	32.05	1043	-	2.90	2.90	0.277	4.74
115	2.90	1.71	1057	12.30	1006	-	0.93	0.93	0.092	1.57
116	2.90	1.70	4757	43.50	996	-	4.28	4.28	0.428	7.28
117	2.90	1.70	2561	23.4	1107	-	4.00	4.00	0.36	6.12
118	2.90	1.72	664	6.15	984	-	0.61	0.61	0.062	1.07
119	2.50	1.705	1847	15.7	1012	-	1.68	1.68	0.166	2.83
120	2.50	1.70	8816	74.9	1047	-	6.46	6.46	0.612	10.4
121	2.50	1.705	3660	31.2	1208	-	2.83	2.83	0.233	3.97
122	2.50	1.71	2492	21.3	404	-	0.88	0.88	0.217	3.71
123	2.50	1.71	1610	13.8	1227	-	1.32	1.32	0.108	1.85
124	2.50	1.76	687	6.05	1239	-	0.505	0.505	0.041	0.72

$F = (I_2)^{\frac{1}{2}}(C_2H_6)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity:- Runs 113 to 120, 122 and 123 = 10^{-7} amp.

Run 121 = 3×10^{-7} amp.

The detector sensitivity refers to that detector current which would produce full scale deflection on the recording system.

Plot for determination of k_2:- Figure 13

Table IV.2

Iodine + Ethane - 295.2°C (568.4°K)

Run	$(I_2)x10^7$ moles/cc	$(C_2H_6)x10^6$ moles/cc	Time(t) secs.	$Fx10^7$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $x10^9$ moles/cc
105	2.06	1.68	2058	15.70	1081	-	2.36	2.36	0.22	3.66
106	2.06	1.71	1746	13.55	1077	-	2.45	2.45	0.23	3.89
107	2.37	1.70	2860	23.70	1213	-	4.60	4.60	0.38	6.45
108	2.37	1.71	3591	29.90	1134	-	4.53	4.53	0.40	6.81
109	2.765	1.68	2098	18.50	987	-	2.38	2.38	0.24	4.05
110	2.765	1.67	1301	1140	1011	-	1.49	1.49	0.15	2.46
111	2.765	1.67	1256	11.00	1015	-	1.40	1.40	0.14	2.30
112	2.765	1.67	716	6.29	982	-	0.79	0.79	0.080	1.34
113	2.765	1.67	390	3.43	996	-	0.47	0.47	0.048	0.795

$F = (I_2)^{\frac{1}{2}}(C_2H_6)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector Sensitivity = 10^{-7} amp.

Plot for determination of k_2:- Figure 13

Table IV.3

Iodine + Ethane - 301.0°C (574.2°K)

Run	$(I_2)x10^7$ moles/cc^{-1}	$(C_2H_6)x10^6$ moles/cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $x10^9$ moles/cc^{-1}
94	2.55	1.56	2262	17.80	954	-	3.80	3.80	0.40	6.19
95	2.53	1.56	1290	10.10	896	-	2.02	2.02	0.225	3.51
96	2.55	1.57	600	4.76	914	-	1.01	1.01	0.11	1.73
97	2.55	1.54	903	7.04	902	-	1.63	1.63	0.18	2.78
98	2.55	1.55	1492	11.7	910	-	2.78	2.78	0.305	4.72
99	1.92	1.65	2593	18.7	1005	-	3.80	3.80	0.38	6.22
100	1.92	1.655	1902	13.8	949	-	3.17	3.17	0.33	5.50
101	1.92	1.655	1377	9.83	997	-	2.42	2.42	0.24	4.01
102	1.92	1.67	628	4.59	942	-	1.20	1.20	0.13	2.10
103	1.92	1.66	1112	8.08	899	-	1.80	1.80	0.20	3.31
104	1.92	1.67	1103	8.07	1130	-	2.10	2.10	0.185	3.09

$F = (I_2)^{\frac{1}{2}}(C_2H_6)t$ (moles/cc^{-1})$^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Plot for determination of k_2:- Figure 13

Table IV.4

Iodine + Ethane - 306.3°C(579.5°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_2H_6)x10^6$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $x10^9$ moles cc^{-1}
85	2.49	1.43	1002	7.15	890	-	2.23	2.23	0.25	3.54
86	2.49	1.42	2381	16.90	965	-	4.89	4.89	0.50	7.15
87	2.49	1.44	1821	13.10	943	-	4.49	4.49	0.47	6.82
88	2.49	1.41	1515	10.65	900	-	3.42	3.42	0.38	5.34
89	2.49	1.42	577	4.09	900	-	1.38	1.38	0.15	2.18
90	2.02	1.61	1535	11.10	330	-	1.16	1.16	0.49	7.81
91	2.02	1.62	2475	18.0	1040	-	5.7	5.7	0.55	8.8
92	2.02	1.63	1335	9.77	1041	-	3.17	3.17	0.30	4.95
93	2.16	1.67	626	4.86	1067	-	1.52	1.52	0.14	2.39

$F = (I_2)^{\frac{1}{2}}(C_2H_6)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity:-

Runs 84 to 88 and 90 to 92 = 10^{-7} amp.

Run 89 = 3×10^{-7} amp.

Peak areas measured by integrator.

Plot for determination of k_2:- Figure 13

FIGURE-13 IODINE + ETHANE

Table IV.5

Iodine + Ethane - 310.9°C (584.1°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_2H_6)x10^6$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $x10^9$ moles cc^{-1}
76	2.77	1.28	1051	7.08	795	-	3.015	3.015	0.38	4.84
77	1.84	1.34	1861	10.7	860	-	5.07	5.07	0.59	7.86
78	1.84	1.35	980	5.675	880	-	2.70	2.70	0.31	4.13
79	1.84	1.34	940	5.40	900	-	2.67	2.67	0.30	3.97
80	1.84	1.34	650	3.74	885	-	1.57	1.57	0.18	2.37
81	2.00	1.40	3973	24.9	786	-	10.7	10.7	1.34	18.8
82	2.00	1.38	889	5.48	875	-	2.54	2.54	0.29	4.00
83	2.00	1.38	1311	8.09	1035	-	3.85	3.85	0.37	5.11
84	2.00	1.39	1805	11.2	956	-	5.45	5.45	0.57	7.89

$F = (I_2)^{\frac{1}{2}}(C_2H_6)t$ (moles cc^{-1})$^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by ingegrator.

Plot for determination of k_2:- Figure 14

Table IV.6

Iodine + Ethane - 314.3°C (587.5°K)

Run	$(I_2)\times10^7$ moles cc^{-1}	$(C_2H_6)\times10^6$ moles cc^{-1}	Time(t) secs.	$F\times10^7$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $\times10^9$ moles cc^{-1}
59	2.54	0.988	2722	13.55	627	-	5.30	5.30	0.84	8.29
60	2.54	0.947	2155	10.30	656	-	3.76	3.76	0.57	5.39
61	2.46	0.925	1588	7.29	666	-	1.66	1.66	0.25	2.30
62	2.54	0.966	1204	5.86	644	-	2.38	2.38	0.37	3.56
63	2.54	0.966	886	4.31	652	-	2.06	2.06	0.315	3.05
64	2.02	1.10	1340	6.62	679	-	2.07	2.07	0.30	3.34
65	2.02	1.11	1849	9.21	700	-	3.37	3.37	0.48	5.27
66	2.02	1.11	903	4.50	700	-	1.31	1.31	0.19	2.08
67	2.02	1.10	570	2.815	715	-	0.71	0.71	0.10	1.09
68	3.79	0.980	1190	7.18	723	-	2.66	2.66	0.37	3.60
69	3.74	0.986	1470	8.87	737	-	3.94	3.94	0.53	5.25
70	2.29	1.03	1011	4.98	680	-	1.95	1.95	0.29	2.94
71	2.29	1.03	1227	6.05	649	-	1.92	1.92	0.29	3.02
72	2.29	1.00	1386	6.63	677	-	2.72	2.72	0.40	3.97
73	2.13	1.305	2065	12.4	841	-	5.12	5.12	0.61	8.00
74	2.13	1.305	847	5.10	820	-	2.17	2.17	0.26	3.45
75	2.13	1.31	615	3.72	807	-	1.80	1.80	0.22	2.85

$F = (I_2)^{\frac{1}{2}} (C_2H_6)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector Sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Plot for determination of k_2:- Figure 14

Table IV.7

Iodine + Ethane - 308.6°C (581.8°K)

Run	$(I_2)\times10^7$ moles cc^{-1}	$(C_2H_6)\times10^6$ moles cc^{-1}	Time(t) secs.	$F\times10^7$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $\times10^9$ moles cc^{-1}
125	2.01	1.03	1895	8.75	790	-	3.31	3.31	0.418	4.19
126	2.01	1.04	890	4.15	810	-	1.47	1.47	0.181	1.88
127	2.01	1.08	785	3.80	792	-	1.65	1.65	0.208	2.24
128	2.01	1.08	780	3.77	737	-	1.52	1.52	0.206	2.22
129	2.43	1.03	2000	10.15	783	-	4.68	4.68	0.594	6.12
130	2.43	1.045	1140	5.87	757	-	2.35	2.35	0.310	3.24
131	2.43	1.045	613	3.16	766	-	1.30	1.30	0.170	1.77
132	2.43	1.045	903	4.66	784	-	1.96	1.96	0.250	2.61

$F = (I_2)^{\frac{1}{2}} (C_2H_6)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Plot for determination of k_2:- Figure 14.

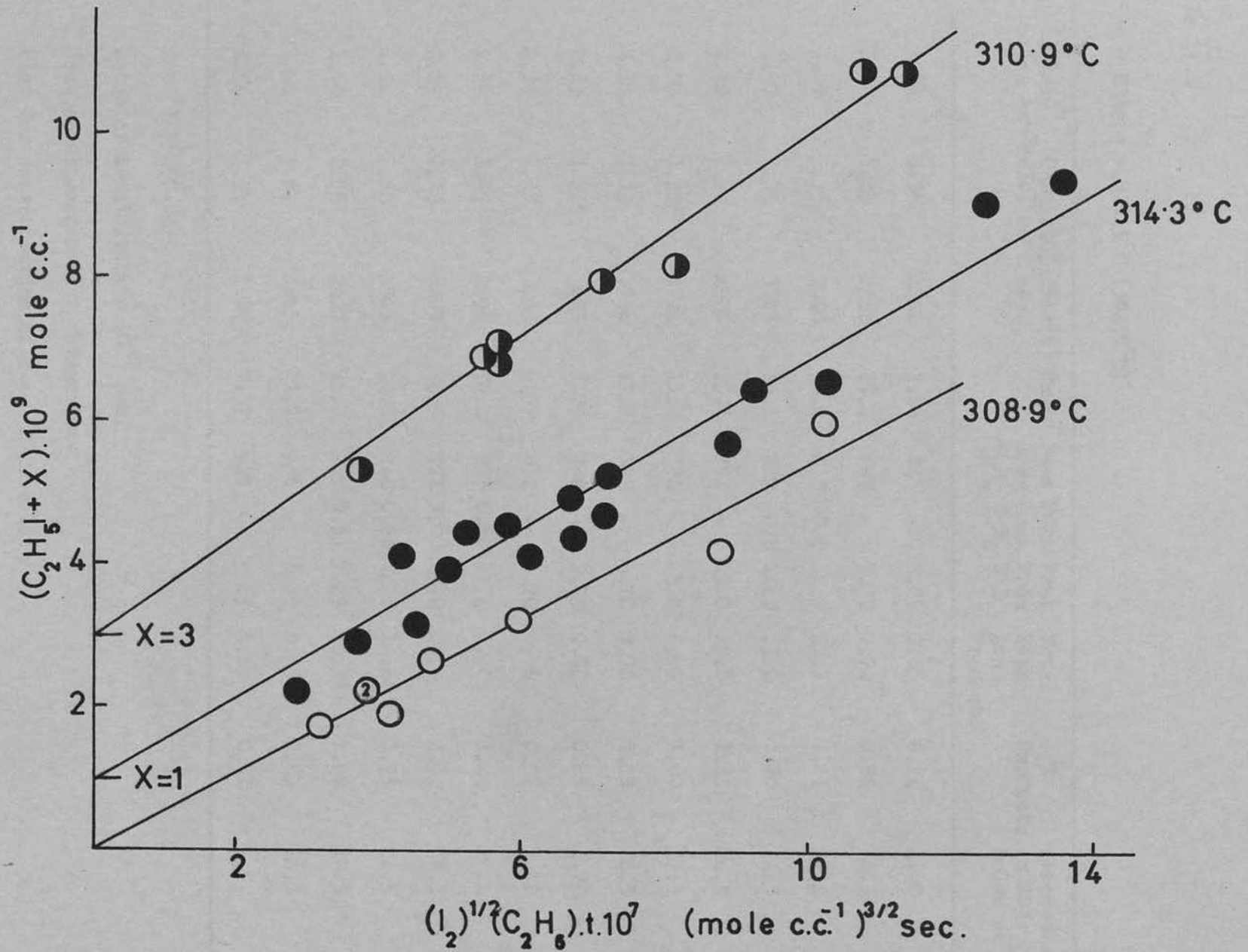


FIGURE-14 IODINE + ETHANE

Table IV.8

Iodine + Ethane - 321.5°C (594.7°K)

Run	$(I_2)\times10^7$ moles cc^{-1}	$(C_2H_6)\times10^6$ moles cc^{-1}	Time(t) secs.	$F\times10^7$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $\times 10^9$ moles cc^{-1}
1	1.21	1.35	1120	5.26	845	-	2.85	2.85	0.34	4.60
2	3.37	1.45	1358	11.4	897	-	7.72	7.72	0.85	12.3
3	1.97	1.33	2680	15.8	815	0.8	12.5	13.3	1.61	21.4
4	1.97	1.35	3183	19.1	819	0.8	14.2	15.0	1.80	24.3
5	2.19	1.34	4006	25.1	794	-	15.0	15.0	1.85	24.8
6	2.19	1.335	1793	11.2	790	-	8.00	8.00	1.00	13.3
7	2.19	1.34	1776	11.1	798	-	8.70	8.70	1.08	14.5
8	2.19	1.345	602	3.79	790	-	2.75	2.75	0.35	4.70
9	2.19	1.33	1055	6.57	814	-	4.70	4.70	0.57	7.60
10	2.19	1.35	2595	16.4	819	0.60	11.4	12.0	1.44	19.4
11	2.19	1.32	6239	38.5	771	3.00	20.0	23.0	2.9	38.3
12	1.54	1.58	3565	22.1	948	0.88	14.0	14.88	1.55	24.5
13	1.54	1.58	2428	15.0	949	0.51	9.85	10.36	1.08	17.1
14	1.54	1.58	1805	11.2	936	-	8.35	8.35	0.89	14.1
15	1.54	1.57	1197	7.37	927	-	5.65	5.65	0.61	9.5

$F = (I_2)^{\frac{1}{2}} (C_2H_6)t$

Detector Sensitivity = 10^{-7} amp.

Peak areas measured by integrator.

Plot for determination of k_2:- Figure 15.

Table IV.9

Iodine + Ethane - 322.7°C (595.9°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_2H_6)x10^6$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $x10^9$ moles cc^{-1}
133	3.34	1.21	1317	9.21	685	-	6.3	6.3	0.912	10.3
134	3.34	1.20	445	3.09	678	-	2.0	2.0	0.294	3.53
135	3.34	1.21	630	4.41	684	-	2.28	2.28	0.332	4.02
136	3.34	1.15	935	5.97	609	-	4.57	4.57	0.744	8.56
137	3.34	1.22	1265	8.92	627	-	6.02	6.02	0.951	11.6
138	3.34	1.21	825	5.77	606	-	3.64	3.64	0.597	7.22
139	3.31	1.24	610	4.35	609	-	3.12	3.12	0.510	6.32
140	2.64	1.45	655	4.88	612	-	2.87	2.87	0.467	6.77
141	2.64	1.43	915	6.725	649	-	4.39	4.39	0.672	9.61
142	2.64	1.43	1995	14.66	653	-	9.47	9.47	1.43	20.4
143	2.64	1.43	1245	9.15	674	-	6.11	6.11	0.898	12.8
144	2.64	1.44	905	6.70	655	-	4.84	4.84	0.733	10.55

$F = (I_2)^{\frac{1}{2}} (C_2H_6)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Plot for determination of k_2:- Figure 15

Table IV.10

Iodine + Ethane - 326.8°C (600.0°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_2H_6)x10^6$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area C_2H_6	Peak Area C_2H_6	Peak Area EtI	Total Peak Area Products	% Products	(Products) $x10^9$ moles cc^{-1}
16	2.70	1.06	1391	7.67	668	0.31	7.19	7.50	1.11	11.7
17	2.70	1.11	3605	33.0	661	2.5	18.4	20.9	3.07	34.1
18	2.70	1.09	2425	13.75	668	0.99	11.7	12.69	1.86	20.3
19	2.70	1.09	1879	10.65	659	0.76	10.5	11.26	1.68	18.3
20	2.70	1.11	692	3.99	660	-	4.15	4.15	0.63	7.0
21	1.63	1.43	1703	9.83	870	0.50	9.15	9.65	1.10	15.7
22	1.63	1.44	837	4.87	887	-	5.09	5.09	0.57	8.20
23	1.63	1.45	4609	27.0	870	1.59	15.5	17.09	1.93	28.0
24	1.60	1.43	3090	17.7	863	1.58	14.6	16.18	1.83	26.1
25	1.63	1.45	1212	6.94	871	-	7.15	7.15	0.81	11.7

$F = (I_2)^{\frac{1}{2}} (C_2H_6)t$ (moles cc^{-1})$^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Plot for determination of k_2:- Figure 15

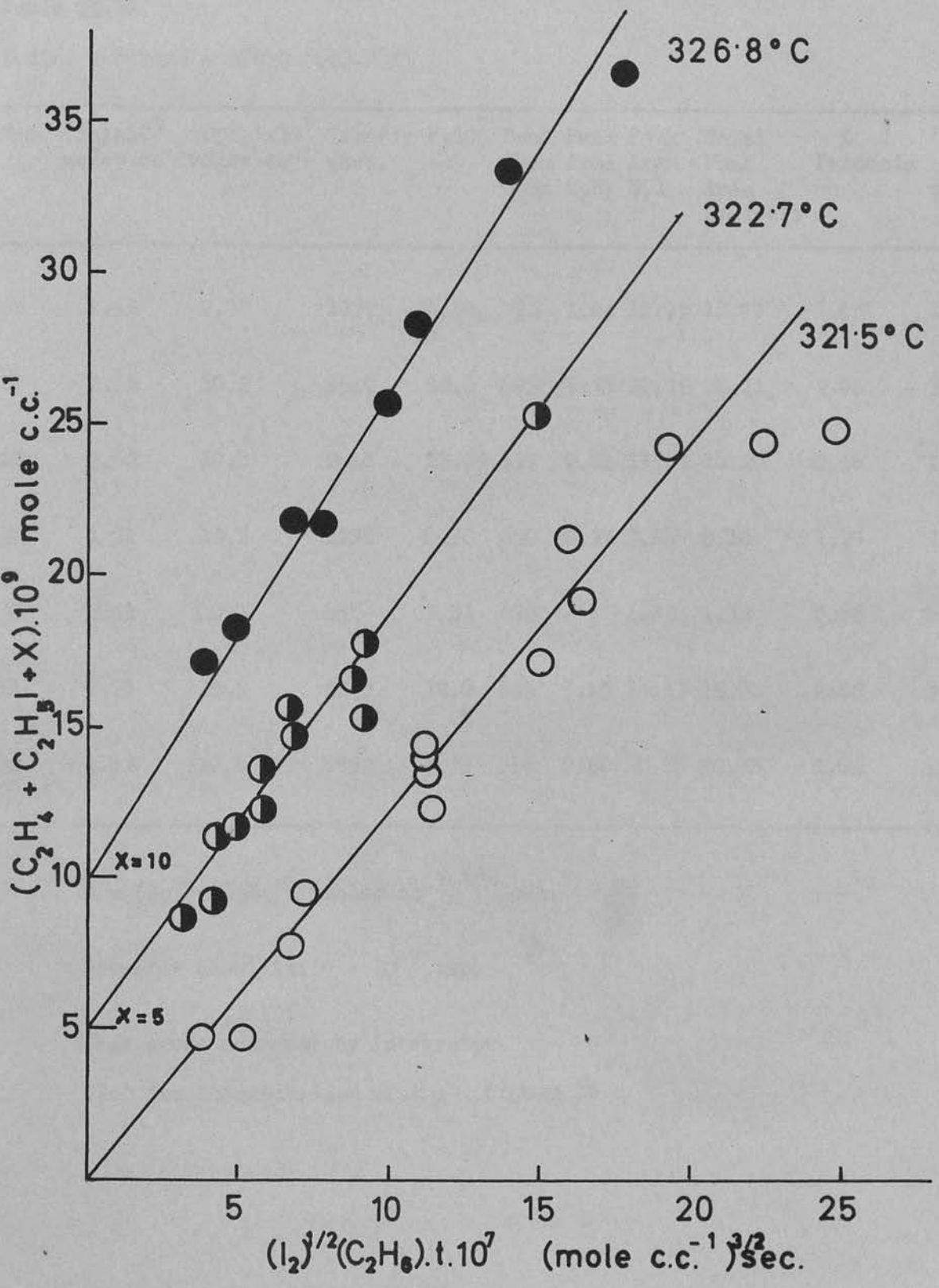


FIGURE-15 IODINE + ETHANE

Table IV.11

Iodine + Ethane - 330°C (603.2°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_2H_6)x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $x10^9$ moles cc^{-1}
26	2.52	9.97	1877	9.39	712	1.04	10.95	11.99	1.65	16.5
27	2.52	10.2	3540	18.1	693	3.33	17.78	21.11	2.96	30.2
28	2.52	10.3	2640	13.65	619	2.61	13.65	16.26	2.56	26.4
29	2.52	10.2	1230	6.30	620	0.27	7.83	8.10	1.29	13.2
30	2.52	10.1	654	3.31	630	-	4.32	4.32	0.68	6.9
31	1.73	10.5	4240	18.6	629	3.25	15.43	18.68	2.88	30.2
32	1.62	10.6	1952	8.33	656	0.80	10.15	10.95	1.64	17.4

$F = (I_2)^{\frac{1}{2}} (C_2H_6)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak areas measured by integrator.

Plot for determination of k_2:- Figure 16

Table IV.12

Iodine + Ethane - 331.3°C (604.7°K)

Run	$(I_2) \times 10^7$ moles cc^{-1}	$(C_2H_6) \times 10^6$ moles cc^{-1}	Time(t) secs.	$F \times 10^7$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $\times 10^9$ moles cc^{-1}
33	1.62	1.07	1892	8.14	608	0.93	10.78	11.71	1.89	20.2
34	2.23	0.695	2510	8.23	439	1.27	10.99	12.26	2.7	18.8
35	2.23	0.70	1295	4.28	432	0.39	5.86	6.25	1.45	10.2
36	2.23	0.68	598	2.13	415	-	2.52	2.52	0.60	4.11
37	2.23	0.71	880	2.95	417	0.05	4.13	4.18	0.99	7.03
38	1.62	0.90	915	3.36	564	-	4.35	4.35	0.765	6.91
39	1.11	0.92	1730	5.32	579	0.415	6.15	6.57	1.14	10.5
40	1.62	0.92	463	1.71	565	-	2.54	2.54	0.45	4.13

$F = (I_2)^{\frac{1}{2}} (C_2H_6)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Plot for determination of k_2:- Figure 16

Table IV.13

Iodine + Ethane - 336.2°C (609.4°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_2H_6)x10^7$ moles cc^{-1}	Time (t) secs.	$Fx10^7$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Product Peak Area	% Products	(Products) $x10^9$ moles cc^{-1}
41	1.92	8.92	575	2.25	525	0.25	3.80	4.05	0.77	6.83
42	1.92	8.90	941	3.67	551	0.39	6.86	7.25	1.30	11.6
43	1.83	8.84	1260	4.78	564	0.68	8.80	9.48	1.65	14.6
44	1.92	9.03	1558	6.16	545	1.46	11.66	13.12	2.35	21.2
45	1.92	9.13	1874	7.16	539	1.77	13.65	15.42	2.79	25.3
46	1.92	4.95	707	1.53	1149	0.39	10.58	10.97	0.945	4.68
47	1.92	5.08	1260	2.80	1124	1.65	19.21	20.86	1.82	9.29
48	1.92	5.13	1467	3.30	1130	2.31	23.1	25.41	2.2	11.3
49	1.92	5.11	867	1.90	1123	0.83	13.88	14.71	1.29	6.61

$F = (I_2)^{\frac{1}{2}} (C_2H_6)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector Sensitivity:-

Runs 40 to 44 = 10^{-7} amp.

Runs 45 to 48 = 3×10^{-8} amp.

Peak Areas measured by integrator.

Plot for determination of k_2:- Figure 16

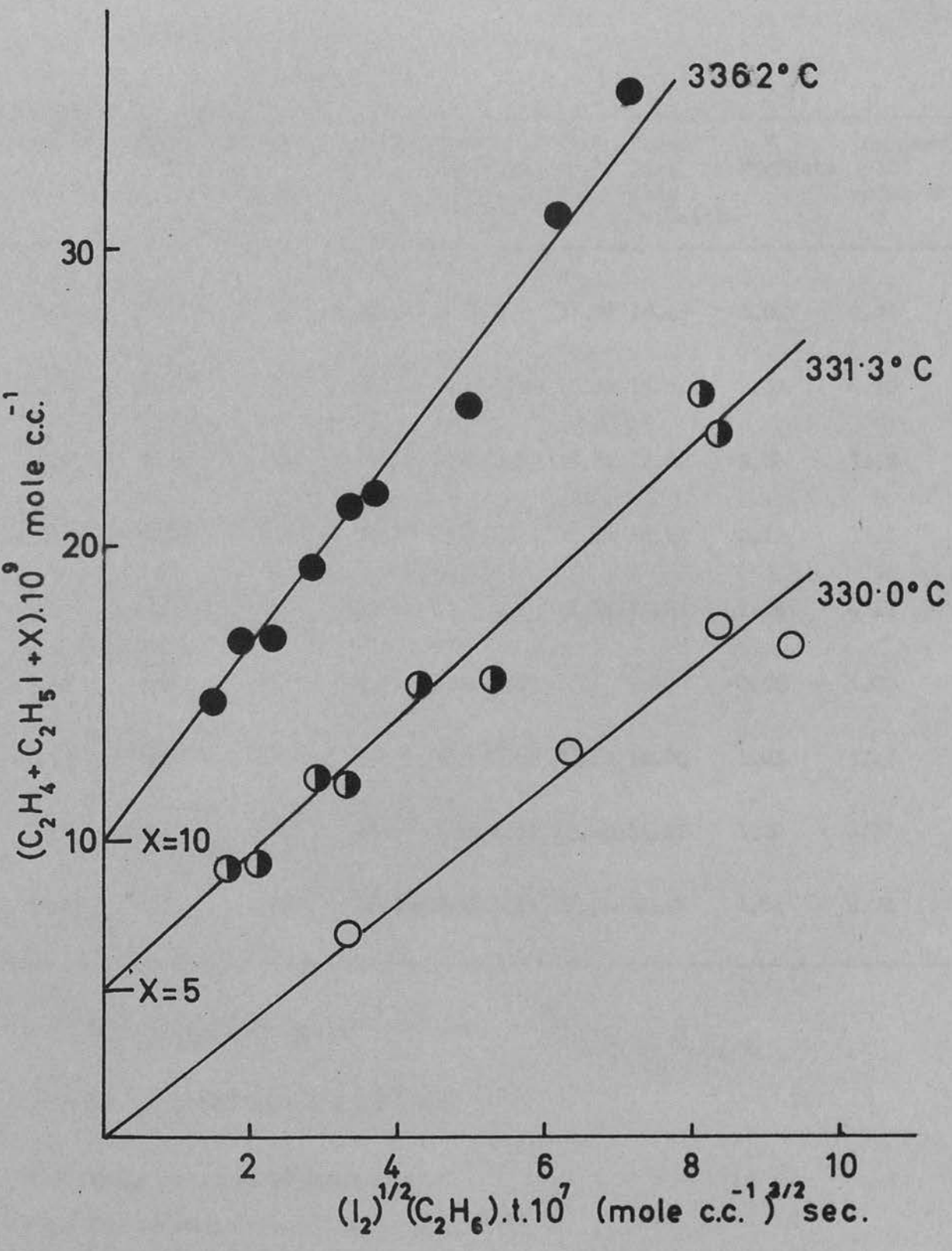


FIGURE - 16 IODINE + ETHANE

Table IV.14

Iodine + Ethane - 340.4°C (613.6°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_2H_6)x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^8$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $x10^9$ moles cc^{-1}
50	1.75	5.12	928	19.9	1118	1.44	16.99	18.43	1.62	8.32
51	1.75	4.86	938	19.05	1172	1.23	14.41	15.64	1.31	6.40
52	1.75	5.12	1647	35.25	1103	3.98	28.84	32.82	2.89	14.8
53	1.75	5.25	1196	26.25	1223	2.31	24.23	26.54	2.12	11.1
54	1.75	5.33	620	13.8	1285	1.74	13.13	14.87	1.15	6.11
55	1.75	5.20	355	7.72	1272	0.07	7.31	7.38	0.58	3.00
56	1.25	5.20	659	12.1	1044	0.68	10.32	11.00	1.04	5.42
57	1.25	5.25	948	17.6	1168	0.99	13.28	14.27	1.20	6.33
58	1.25	5.33	1231	18.45	1169	1.97	17.49	19.46	1.64	8.74

$F = (I_2)^{\frac{1}{2}} (C_2H_6)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 3×10^{-8} amp.

Peak Areas measured by integrator.

Plot for determination of k_2:- Figure 17

Table IV.15

Iodine + Ethane - 344.2°C (617.4°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_2H_6)x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^8$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $x10^9$ moles cc^{-1}
175	1.48	4.42	751	12.8	937	1.11	11.48	12.59	1.32	5.84
176	1.48	4.49	960	16.6	965	1.81	18.32	20.13	2.04	9.15
177	1.48	4.49	591	10.2	981	0.92	12.06	12.98	1.31	5.86
178	1.48	4.42	756	12.9	982	1.05	12.73	13.78	1.38	6.10
179	1.48	4.68	400	7.21	1000	-	8.30	8.30	0.83	3.86
180	1.48	3.48	900	12.1	761	1.38	10.85	12.23	1.58	5.51
181	1.48	3.48	1284	17.2	785	2.58	16.90	19.48	2.43	8.44
182	1.48	3.64	641	8.98	793	0.85	9.61	10.46	1.30	4.74

$F = (I_2)^{\frac{1}{2}} (C_2H_6)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector Sensitivity = 3×10^{-8} amp.

Peak Areas measured by integrator.

Plot for determination of k_2:- Figure 17

Table IV.16

Iodine + Ethane - 339.4°C (612.6°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_2H_6)x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $x10^9$ moles cc^{-1}
145	1.91	6.39	3527	9.85	490	4.37	19.68	24.05	4.68	29.8
146	1.91	6.26	914	2.50	503	0.45	7.70	8.15	1.59	9.95
147	1.91	6.26	5367	14.68	583	13.10	32.0	45.10	7.18	44.9
148	1.91	6.23	1857	5.06	502	1.61	11.46	13.07	2.54	15.8
149	1.91	6.28	1182	3.24	491	1.95	8.49	10.44	2.08	13.1
150	1.91	6.23	6582	17.92	442	11.21	18.13	29.34	6.23	38.8
151	1.91	6.23	2208	6.01	471	2.03	12.37	14.40	2.97	18.5
152	1.91	6.15	608	1.63	438	Trace	4.18	4.18	0.946	5.82
153	1.91	6.23	274	0.75	492	-	2.46	2.46	0.498	3.10
154	1.20	9.40	7520	24.46	586	11.0	14.59	25.59	4.18	39.3
155	1.20	9.50	3632	11.94	626	3.31	9.81	13.12	2.05	19.5
156	1.20	9.45	6294	20.58	622	7.77	15.28	23.05	3.57	33.7

$F = (I_2)^{\frac{1}{2}} (C_2H_6)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Plot for determination of k_2:- Figure 17

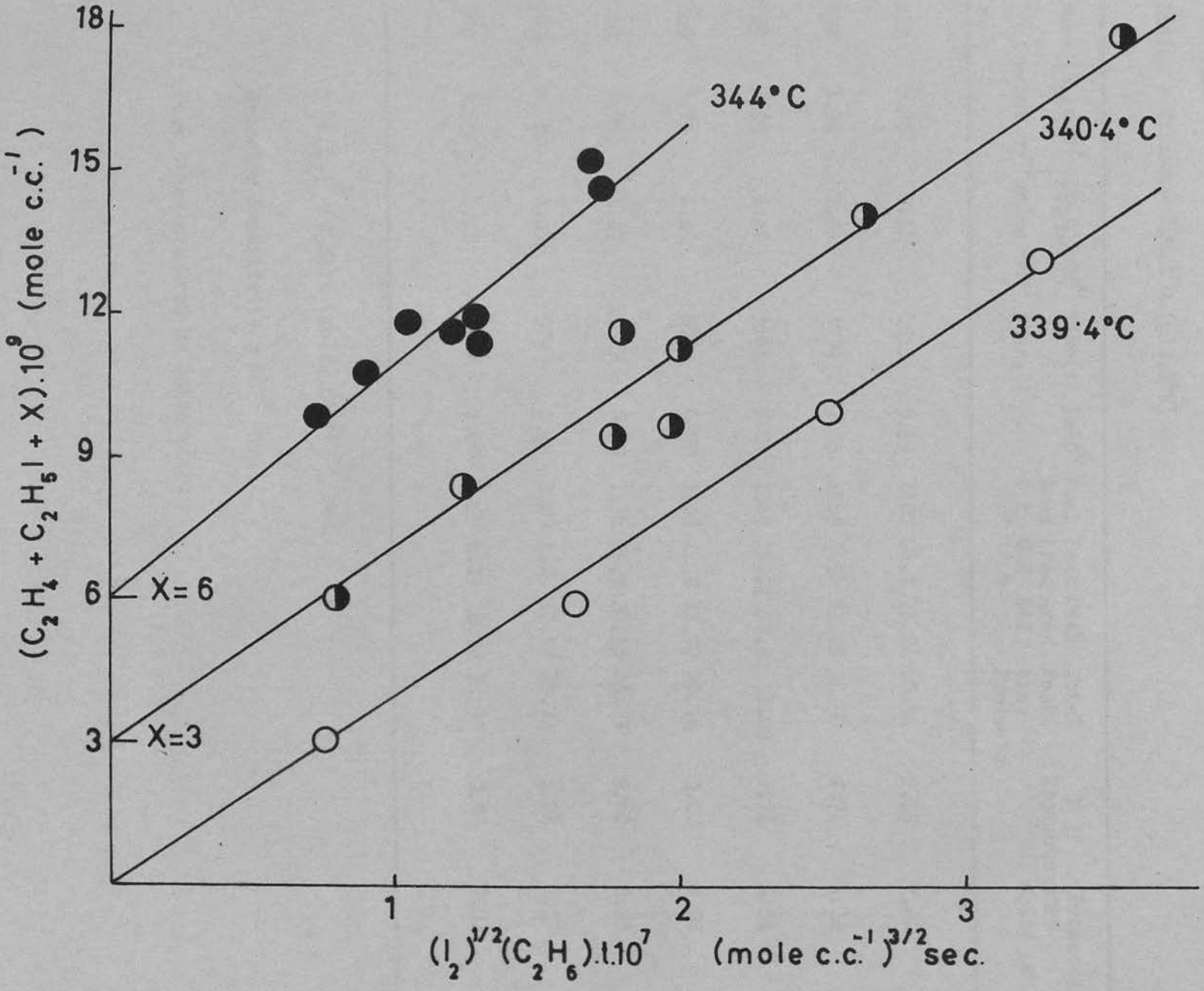


FIGURE-17 IODINE + ETHANE

Table IV.17

Iodine + Ethane - 339.1°C (612.3°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_2H_6)x10^6$ moles cc^{-1}	Time(t) secs.	$Fx10^6$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $x10^8$ moles cc^{-1}
157	3.35	1.51	6853	5.99	1107	26.7	33.84	60.54	5.18	7.82
158	3.35	1.51	1779	1.55	1368	4.56	34.03	38.59	2.74	4.14
159	3.35	1.48	3564	3.05	1365	15.24	37.84	53.08	3.74	5.54
160	3.35	1.49	808	0.70	1425	1.48	18.70	20.18	2.07	3.08
161	3.35	1.47	10318	8.78	1436	55.7	29.53	85.23	5.60	8.23
162	3.35	1.47	579	0.49	1283	1.2	12.54	13.74	1.04	1.53
163	3.35	1.48	1867	1.60	1289	6.19	28.78	34.97	2.53	3.74

$F = (I_2)^{\frac{1}{2}} (C_2H_6)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector Sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Table IV.18

Iodine + Ethane - Reactions in packed vessel.

309.0°C (582.2°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_2H_6)x10^6$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $x10^9$ moles cc^{-1}
164	2.48	1.18	1044	6.13	922	-	1.60	1.60	0.17	2.01
165	2.48	1.20	1506	9.00	924	1.80	2.46	4.26	0.46	5.51
166	2.48	1.215	2693	16.29	931	1.23	4.47	5.70	0.61	7.39
167	2.48	1.18	1061	6.23	1020	-	1.85	1.85	0.18	2.12
168	2.48	1.22	1232	7.48	1027	-	2.80	2.80	0.27	3.29
169	2.48	1.23	2236	13.70	348	-	1.30	1.30	0.37	4.55
170	2.48	1.23	816	5.00	1038	-	1.74	1.74	0.17	2.04

$F = (I_2)^{\frac{1}{2}} (C_2H_6)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity:- Runs 163 to 167 and 169 = 10^{-7} amp.

Run 168 = 3×10^{-7} amp.

Peak Areas measured by integrator.

Table IV.19

Iodine + Ethane - 330.8°C (604.0°K)

- Reactions carried out in packed vessel.

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_2H_6)x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area C_2H_6	Peak Area C_2H_4	Peak Area EtI	Total Peak Area Products	% Products	(Products) $x10^9$ moles cc^{-1}
171	1.94	8.10	512	1.83	489	0.23	1.52	1.75	0.36	2.92
172	1.94	8.23	595	2.16	486	0.63	2.76	3.39	0.69	5.68
173	1.94	7.59	1133	3.79	498	0.36	5.03	5.39	1.07	8.12
174	2.23	9.05	538	2.30	567	Trace	3.08	3.08	0.54	4.89

$F = (I_2)^{\frac{1}{2}} (C_2H_6)t$ (moles cc^{-1})$^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Table IV.20

Iodine + Ethane - Data for Arrhenius Plot

$T^{o}K$	$\frac{1}{T^{o}K} \times 10^{3}$	$k_2 \times 10^{-4}$ cc/mole-sec.	$\log k_2$	$KI_2 \times 10^{8}$ $(moles/cc)^{\frac{1}{2}}$
617.4	1.620	6.67	4.82	78.30
613.6	1.630	5.41	4.73	76.20
612.0	1.634	5.23	4.72	75.10
609.4	1.641	4.75	4.68	69.02
604.5	1.654	3.59	4.56	62.37
603.2	1.658	3.37	4.53	59.12
600.0	1.667	3.03	4.48	54.7
595.5	1.678	2.72	4.43	48.1
594.7	1.681	2.40	4.38	47.9
587.5	1.702	1.41	4.15	39.67
584.1	1.712	2.00	4.30	35.25
581.8	1.719	1.61	4.21	34.0
579.5	1.726	1.66	4.22	31.23
574.2	1.742	1.49	4.17	26.6
568.4	1.759	1.00	4.00	23.5
564.2	1.772	0.709	3.85	2.10
*604.0	1.656	3.67	4.54	60.2
*582.2	1.718	1.19	4.07	34.4

* Reactions carried out in packed vessel.

Arrhenius Plot:- Figure 25

$\log k_2 = (14.23 \pm 0.4) - (26{,}300 \pm 900)/2.303RT$

(c.c. $mole^{-1} sec.^{-1}$)

IV.2 The Reaction of Iodine with Propane in the temperature Range 271°C to 311°C

The following tables give the experimental data for the reaction of iodine with propane. The runs are listed in order of increasing temperature and are numbered in the order they were carried out.

Table IV.21/

Table IV.21 Iodine + Propane - 271.3°C (544.5°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_3H_8)x10^6$ moles cc^{-1}	Time(t) secs.	$Fx10^6$	Peak Area C_3H_8	Peak Area C_3H_6	Peak Area iPrI	Peak Area nPrI	Total Peak Area Products	% Products	(Products) $x10^9$ moles cc^{-1}
67	3.80	1.285	3630	2.87	47.2	0.278	0.03	0.014	0.322	0.68	8.70
68	3.80	1.28	3050	2.405	50.4	0.233	0.031	0.014	0.278	0.55	7.00
69	3.80	1.28	2415	1.90	48.6	0.195	0.027	0.009	0.231	0.47	6.00
70	3.80	1.27	1665	1.30	49.4	0.110	0.026	0.007	0.143	0.29	3.70
71	2.59	1.87	3605	3.43	77.4	0.336	0.030	0.018	0.384	0.495	9.25
72	2.09	1.89	3524	3.04	74.8	0.283	0.026	0.014	0.324	0.43	8.10
73	4.95	1.81	1945	2.48	72.8	0.171	0.038	0.013	0.222	0.30	5.50
74	2.59	1.86	2070	1.96	74.8	0.170	0.032	0.010	0.202	0.27	5.00
75	2.59	1.88	2485	2.38	75.2	0.233	0.035	0.015	0.283	0.375	7.10
76	2.59	1.88	2010	1.92	71.0	0.170	0.033	0.011	0.214	0.30	5.6

$F = (I_2)^{\frac{1}{2}} (C_3H_8)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 3×10^{-7} amp.

Peak Areas measured by planimeter.

Plot for the determination of k_2:- Figure 18

Table IV.22 Iodine + Propane - 280.8°C (554.0°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_3H_8)x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area C_3H_8	Peak Area C_3H_6	Peak Area iPrI	Peak Area nPrI	Total Peak Area Products	% * Products	(Products) $x10^9$ moles cc^{-1}
20	3.71	5.77	3550	12.5	640	9.38	0.22	0.26	9.86	1.20	6.92
21	3.71	5.39	1811	5.94	571	5.46	0.25	0.14	5.85	0.69	3.72
22	2.955	4.955	1520	4.10	522	4.65	0.23	0.11	4.99	0.63	3.12
23	2.955	4.955	1261	3.40	522	3.80	0.23	0.16	4.19	0.48	2.40
24	2.955	5.07	991	2.73	522	3.27	0.26	0.13	3.66	0.38	1.95
25	2.955	5.24	558	1.59	530	2.82	0.37	0.10	3.29	0.30	1.57
26	2.11	6.17	1735	4.91	644	5.08	0.27	0.22	5.57	0.54	3.33
27	2.32	6.29	705	2.14	630	3.11	0.26	0.09	3.46	0.23	1.49
28+	2.32	6.49	1350	4.22	662	4.36	0.29	0.16	4.81	0.40	2.60
29+	2.11	6.40	1959	5.75	695	5.19	0.27	0.23	5.69	0.48	3.07
30+	2.32	6.52	970	3.05	678	3.62	0.33	0.16	4.11	0.28	1.83
31+	2.67	6.46	2370	7.91	650	6.38	0.365	0.31	7.05	0.75	4,85
32+	2.11	6.46	784	2.62	694	3.26	0.27	0.175	3.70	0.21	1.36

* 0.32% impurity C_3H_6 subtracted.

$F = (I_2)^{\frac{1}{2}} (C_3H_8)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

\+ Reaction Temperature = 280.2°C (553.4°K)

Plot for the determination of k_2:- Figure 18

Table IV.23 Iodine + Propane - 285.7°C (558.9°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_3H_8)x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area C_3H_8	Peak Area C_3H_6	Peak Area iPrI	Peak Area nPrI	Total Peak Area Products	% * Products	(Products) $x10^9$ moles cc^{-1}
33	2.56	6.26	838	2.655	660	4.78	0.33	0.11	5.22	0.48	3.01
34	2.56	6.20	2063	6.47	654	7.81	0.32	0.285	8.42	0.94	5.83
35	3.68	5.89	935	3.34	615	5.34	0.43	0.18	5.95	0.64	3.77
36	2.56	6.15	1472	4.58	664	6.10	0.31	0.22	6.63	0.67	4.12
37	2.56	6.15	2216	6.90	662	9.12	0.31	0.33	9.76	1.13	6.95
38	2.56	6.55	701	2.32	674	4.17	0.33	0.11	4.61	0.36	2.36
39	1.81	6.49	2098	5.79	691	7.65	0.34	0.25	8.24	0.86	5.58
40	2.91	6.17	1563	5.20	642	6.81	0.38	0.25	7.44	0.82	5.05
41	2.91	6.17	993	3.30	637	5.18	0.42	0.17	5.77	0.58	3.58
42	2.91	6.32	1203	4.10	659	5.86	0.42	0.22	6.50	0.66	4.17
43	2.91	6.17	534	1.78	637	3.77	0.39	0.08	4.24	0.33	1.98

* 0.32% impurity propylene subtracted.

$F = (I_2)^{\frac{1}{2}} (C_3H_8)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Plot for the determination of k_2:- Figure 18

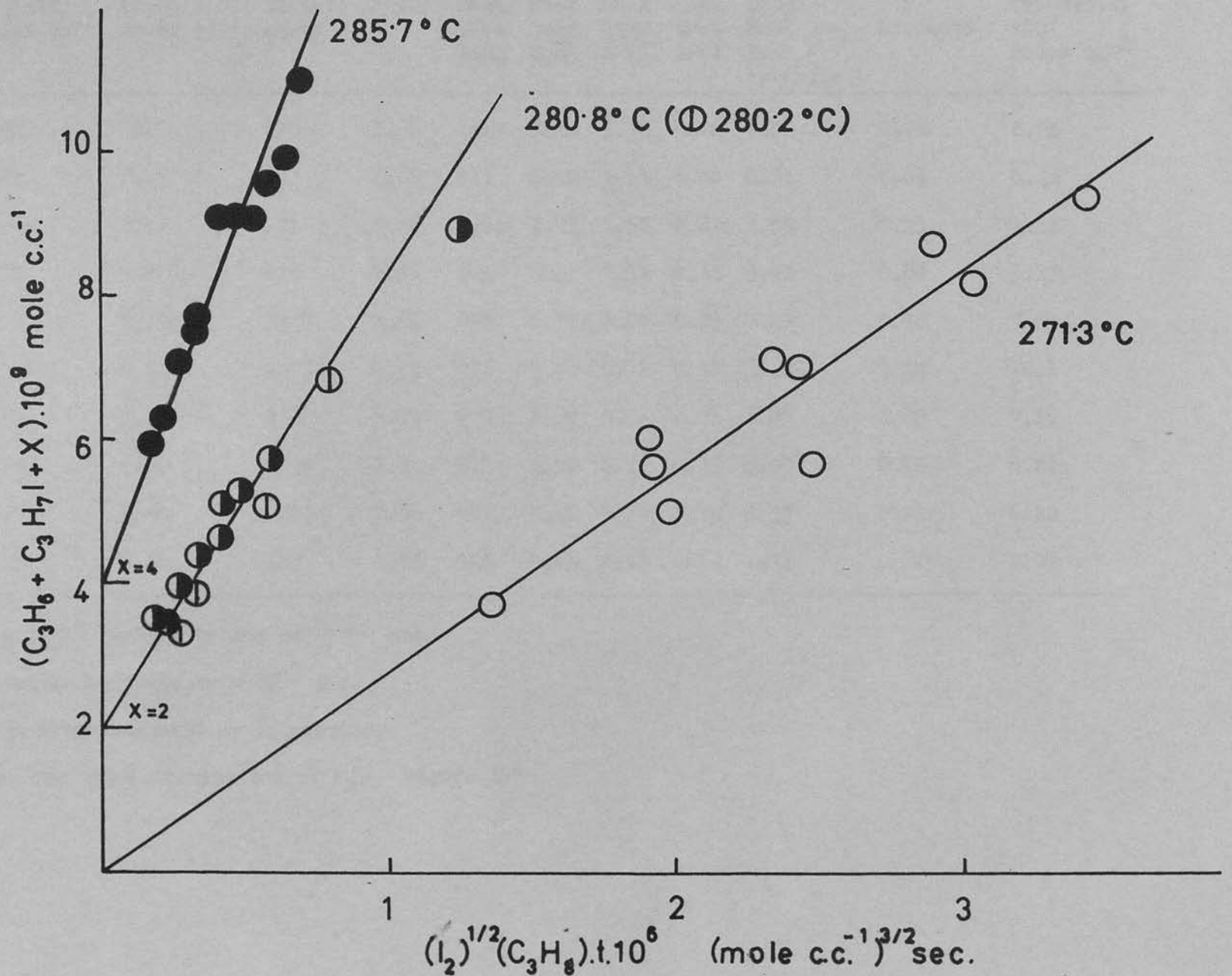


FIGURE-18 IODINE + PROPANE

Table IV.24 Iodine + Propane 294.8°C (568.0°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_3H_8)x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area C_3H_8	Peak Area C_3H_6	Peak Area iPrI	Peak Area nPrI	Total Peak Area Products	% Products	(Products) $x10^9$ moles cc^{-1}
77	2.88	10.3	970	5.36	1149	7.18	1.36	0.46	9.00	0.78	8.04
78	3.09	10.2	710	4.03	991	4.50	1.51	0.30	6.31	0.63	6.42
79	3.09	10.2	475	2.69	1114	2.83	1.50	0.215	4.55	0.41	4.15
80	2.37	7.745	915	3.53	824	4.29	1.12	0.31	5.72	0.69	5.35
81	2.37	7.745	1283	4.84	851	6.77	1.09	0.55	8.41	0.98	7.59
82	1.98	6.84	2410	7.34	738	9.74	0.76	0.53	11.03	1.48	10.1
83	1.98	6.92	1720	5.30	739	7.04	0.71	0.34	8.09	1.08	7.46
84	1.98	6.90	1250	3.84	611	4.52	0.72	0.33	5.57	0.90	6.21
85	2.29	6.84	1205	3.94	711	5.42	0.79	0.32	6.53	0.91	6.22
86	2.18	6.86	480	1.54	728	1.84	0.76	0.14	2.74	0.375	2.57

$F = (I_2)^{\frac{1}{2}} (C_3H_8)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Plot for the determination of k_2:- Figure 19

Table IV.25 Iodine + Propane - 298.9°C (572.1°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_3H_8)x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area C_3H_8	Peak Area C_3H_6	Peak Area iPrI	Peak Area nPrI	Total Peak Area Products	% * Products	(Products) $x10^9$ moles cc^{-1}
44	2.86	5.19	1184	3.29	558	10.6	0.58	0.42	11.60	1.72	8.94
45	2.86	5.415	1273	3.69	553	11.4	0.59	0.45	12.44	1.88	10.20
46	2.86	5.47	737	2.16	526	7.02	0.64	0.32	7.98	1.18	6.45
47	2.05	5.19	1859	4.37	516	13.1	0.53	0.48	14.11	2.34	12.1
48	2.05	5.22	1255	2.97	504	8.76	0.54	0.39	9.69	1.57	8.20
49	2.05	5.22	606	1.43	509	5.34	0.55	0.21	6.10	0.86	4.49
50	2.20	3.43	1511	2.43	365	7.77	0.47	0.34	8.58	1.98	6.80
51	2.20	3.51	880	1.45	360	4.91	0.46	0.17	5.54	1.20	4.21
52	2.20	3.30	600	0.93	364	No Data	0.37	0.10	-	-	-
53	1.26	4.12	456	0.67	397	3.06	0.21	-	3.27	0.50	2.06
54	2.20	3.31	1064	1.65	362	5.34	0.42	0.32	6.08	1.33	4.41
55	2.20	3.01	775	1.09	384	4.08	0.43	0.21	4.72	0.89	2.68
56	2.20	3.51	1315	2.165	372	6.30	0.41	0.29	7.00	1.53	5.18

* 0.32% impurity propylene subtracted.

$F = (I_2)^{\frac{1}{2}}(C_3H_8)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Plot for the determination of k_2:- Figure 19

Table IV.26 Iodine + Propane - 306.7°C (579.9°K)

Run	$(I_2) \times 10^7$ moles cc^{-1}	$(C_3H_8) \times 10^7$ moles cc^{-1}	Time(t) secs.	$F \times 10^7$	Peak Area C_3H_8	Peak Area C_3H_6	Peak Area iPrI	Peak Area nPrI	Total Peak Area Products	% Products	(Products) $\times 10^9$ moles cc^{-1}
87	2.96	7.08	623	2.40	828	5.76	1.87	0.49	8.12	0.97	6.86
88	2.91	7.22	393	1.53	855	3.11	1.72	0.32	5.15	0.60	4.33
89	2.91	7.36	490	1.94	817	4.74	1.71	0.44	7.89	0.96	7.07
90	2.96	7.47	383	1.56	809	3.34	1.73	0.405	5.47	0.67	4.99
91	2.16	6.45	610	1.83	698	4.70	1.25	0.45	6.40	0.91	5.87
92	2.16	6.39	313	0.93	694	1.85	1.15	0.20	3.20	0.46	2.94
93	2.16	6.39	500	1.49	718	4.02	1.20	0.34	5.56	0.77	4.92
94	2.16	6.45	923	2.77	704	7.86	1.35	0.53	9.74	1.37	8.83
95	1.72	16.05	628	4.18	695	3.89	0.97	0.31	5.17	0.74	12.2
96	1.72	16.10	634	4.235	700	4.40	0.88	0.31	5.59	0.79	12.7
97	1.72	4.65	1265	2.44	503	7.90	0.71	0.50	9.11	1.78	8.26
98	1.74	10.80	631	2.26	466	3.07	0.62	0.25	3.94	0.84	9.01

$F = (I_2)^{\frac{1}{2}} (C_3H_8)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity:- Runs 87 to 97 = 10^{-7} amp.

Run 98 = 3×10^{-7} amp.

Peak Areas measured by integrator.

Plot for the determination of k_2:- Figure 19

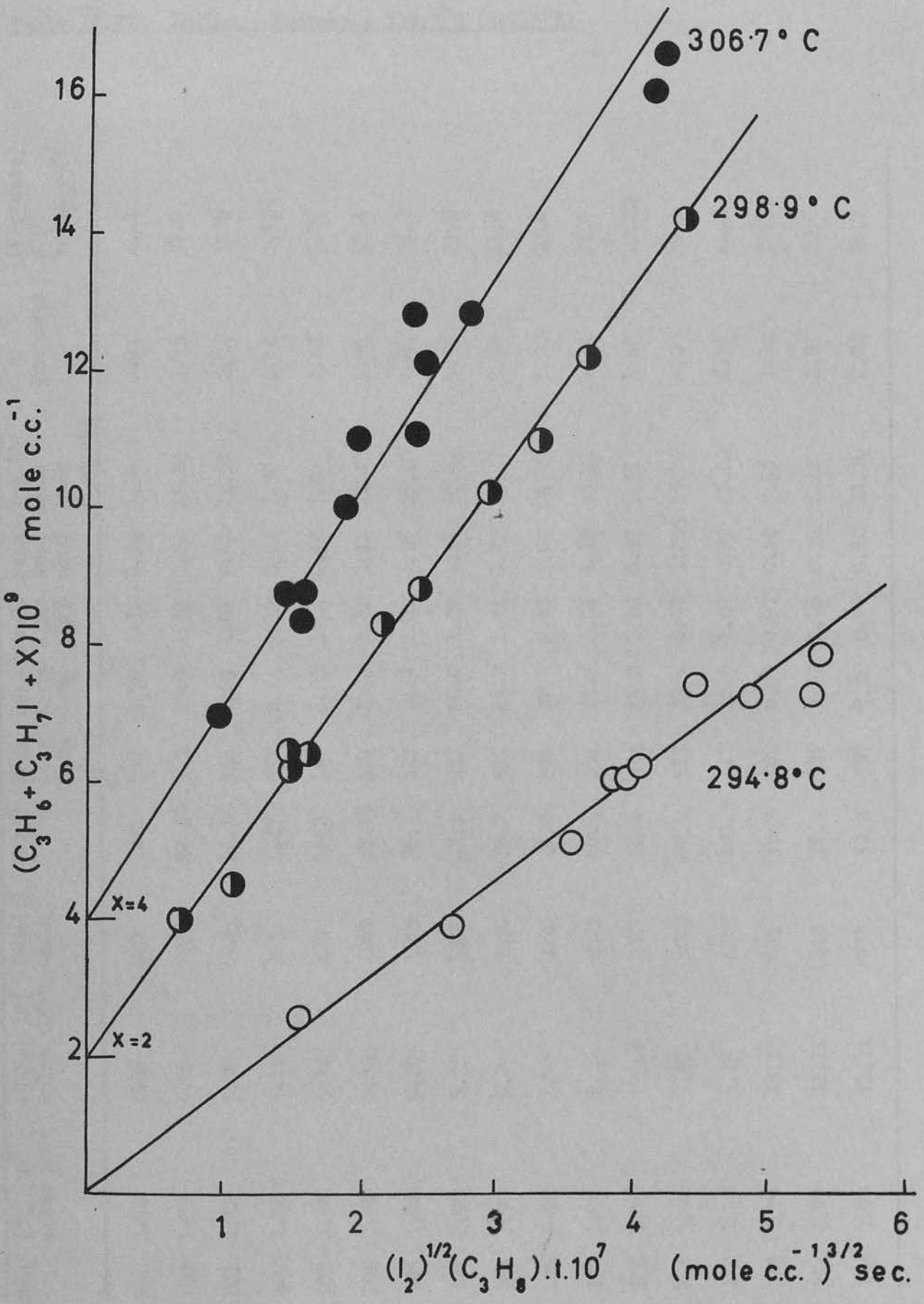


FIGURE- 19 IODINE + PROPANE

Table IV.27 Iodine + Propane - 319.3°C (592.5°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_3H_8)x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^8$	Peak Area C_3H_8	Peak Area C_3H_6	Peak Area iPrI	Peak Area nPrI	Total Peak Area Products	% Products	(Products) $x10^9$ moles cc^{-1}
99	1.98	4.93	320	7.02	567	3.70	1.32	0.34	5.36	0.94	4.41
100	1.98	5.06	905	20.40	562	13.9	1.10	0.84	15.84	2.75	13.9
101	1.98	5.20	608	14.10	543	9.65	1.07	0.61	11.31	2.04	10.6
102	1.98	5.15	195	4.47	553	2.44	1.12	0.24	3.80	0.68	3.52
103	1.98	5.12	430	9.80	547	6.25	1.14	0.47	7.86	1.42	7.25
104	1.98	5.12	1260	28.70	529	19.4	1.01	1.12	21.23	3.79	19.4
105	1.98	5.20	1575	36.4	517	24.1	1.04	1.26	26.40	4.86	25.3
106	1.98	5.23	1850	43.1	513	28.0	1.09	1.25	30.34	5.59	29.2
107	1.98	5.09	3520	79.7	510	43.2	1.14	1.13	45.47	8.19	41.6
108	1.98	4.98	2210	49.0	531	27.3	0.95	1.04	29.29	5.22	26.0
109	1.98	5.17	2525	58.1	514	31.3	1.01	1.10	33.41	6.11	31.6
110	1.79	13.22	401	22.4	544	4.12	1.02	0.37	5.51	1.00	13.22
111	1.98	5.17	3000	69.0	517	33.4	0.97	1.025	35.39	6.40	33.1
112	1.98	5.15	4505	103.2	517	46.6	1.03	0.89	48.52	8.59	44.2
113	1.79	13.11	635	35.2	561	6.02	0.975	0.50	7.50	1.32	17.3
114	1.79	13.11	340	18.9	537	3.23	0.96	0.29	4.48	0.83	10.9
115	1.79	13.11	933	51.7	537	9.80	0.76	0.60	11.16	2.04	26.7

Table IV.27 continued on Page 80.

Table IV.27 Iodine + Propane - 319.3°C (592.5°K) Continued.

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_3H_8)x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^8$	Peak Area C_3H_8	Peak Area C_3H_6	Peak Area iPrI	Peak Area nPrI	Total Peak Area Products	% Product	(Product) $x10^9$ moles cc^{-1}
116	1.79	13.05	980	54.1	540	8.99	0.74	0.59	10.32	1.87	24.3
117	1.79	13.11	309	16.4	543	2.58	0.94	0.24	3.76	0.69	9.06
118	1.79	13.11	1488	82.5	523	13.6	0.70	0.69	14.99	2.78	36.5
119	1.79	13.14	2210	122.8	520	19.2	0.67	0.70	20.57	3.80	49.8
120	1.79	13.14	2771	154.0	523	24.2	0.64	0.60	25.44	4.65	61.2
121	1.79	13.11	3375	187.4	514	26.9	0.61	0.53	28.04	5.22	68.4
122	1.79	13.11	4071	225.7	513	29.8	0.64	0.49	30.95	5.70	74.6
123	1.79	13.11	4895	271.4	508	32.2	0.60	0.41	33.21	6.14	80.5
124	1.98	5.15	5460	125.1	483	51.4	1.18	0.68	53.26	9.90	51.2
125	1.98	5.17	6330	145.6	487	58.2	1.12	0.70	60.02	11.0	56.9
126	1.98	5.23	7215	167.9	478	62.4	1.20	0.67	64.27	11.9	62.1

$F = (I_2)^{\frac{1}{2}} (C_3H_8)t$ (moles cc^{-1}) sec.

Detector sensitivity:- Runs 99 to 109, 111, 112, 125 and 126 = 10^{-7} amp.

Runs 110,113 to 124.

Table IV.28 Iodine + Propane - 319.7°C (592.9°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_3H_8)x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^8$	Peak Area C_3H_8	Peak Area C_3H_6	Peak Area iPrI	Peak Area nPrI	Total Peak Area Products	% * Products	(Products) $x10^9$ moles cc^{-1}
1	2.76	10.0	1670	87.7	1023	57.6	-	-	57.6	5.00	50.0
2	2.76	10.1	1010	53.6	1045	41.8	-	-	41.8	3.52	35.3
3	2.76	4.90	1680	43.2	498	34.8	-	-	34.8	6.21	30.4
4	2.76	4.98	590	15.4	517	15.2	0.86	0.38	16.44	2.73	13.6
5	2.76	5.06	310	8.235	518	8.70	-	-	8.70	1.33	6.84
6	2.76	5.06	426	11.3	533	11.7	0.87	0.44	13.0	2.06	10.4
7	2.76	5.09	226	6.04	525	5.80	0.96	0.27	7.0	1.00	5.09
8	2.76	5.12	375	10.1	519	10.2	1.05	0.43	11.7	1.88	9.60
9	2.76	4.96	259	6.745	541	6.90	0.73	0.42	8.05	1.15	5.70
10	2.76	5.04	502	13.3	507	12.6	0.69	0.50	13.8	2.33	11.7
11	2.76	5.09	1004	26.8	497	23.6	0.80	0.89	25.3	4.52	23.0
12	2.76	4.98	1490	38.95	499	27.2	0.94	1.04	29.2	5.21	25.9
13	2.76	5.04	2592	12.7	488	45.0	1.02	1.09	47.1	8.18	41.2
14	1.60	5.41	586	12.7	540	12.9	0.67	0.57	14.1	2.23	12.1
15	1.60	5.44	407	8.86	543	9.20	0.69	0.39	10.3	1.54	8.36
16	1.60	5.50	381	8.38	561	8.90	0.70	0.39	10.0	1.43	7.86

TableIV.28 Continued on Page 82.

Table IV.28 Iodine + Propane - 319.7°C (592.9°K) Continued

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_3H_8)x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^8$	Peak Area C_3Hg	Peak Area C_3H_6	Peak Area iPrI	Peak Area nPrI	Total Peak Area Products	% * Products	(Products) $x10^9$ moles cc^{-1}
17	1.60	5.36	500	10.7	563	11.9	0.82	0.52	13.2	1.95	10.5
18	1.41	5.55	360	7.49	597	9.0	0.81	0.40	10.2	1.36	7.55
19	0.60	5.77	358	5.06	602	6.50	0.42	0.21	7.10	0.84	4.85

$F = (I_2)^{\frac{1}{2}}(C_3H_8)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector Sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

* 0.32% Propylene subtracted

Plot for the determination of k_2:- Figure 20

Table IV.22 Iodine + Propane 327.7°C (600.9°K)

Run	$(I_2)\times10^7$ moles cc^{-1}	$(C_3H_8)\times10^7$ moles cc^{-1}	Time(t) secs.	$F\times10^8$	Peak Area C_3H_8	Peak Area C_3H_6	Peak Area iPrI	Peak Area nPrI	Total Peak Area Products	% Products	(Products) $\times10^9$ moles cc^{-1}
57	1.95	3.765	655	10.9	363	13.3	1.08	0.89	15.27	3.72*	14.0
58	1.95	3.765	330	5.49	387	8.05	0.87	0.48	9.40	2.05*	7.72
59	1.20	2.67	550	5.08	842	24.7	1.61	1.50	27.81	2.88*	7.69
60	1.28	2.725	355	3.46	869	18.3	2.11	1.31	21.72	2.10*	5.72
61	1.34	2.67	418	4.085	850	15.4	2.18	1.03	18.61	2.14	5.70
62	1.34	2.62	576	5.52	845	22.3	2.02	1.12	25.44	2.93	7.66
63	1.34	2.64	490	4.735	864	19.3	2.22	0.96	22.48	2.54	6.71
64	1.42	2.67	240	2.415	848	9.49	2.56	0.63	12.68	1.47	3.92
65	1.34	2.62	584	5.60	876	23.3	2.23	1.43	26.96	2.98	7.80
66	1.34	2.64	262	2.53	867	10.05	2.32	0.61	12.98	1.47	3.88

* 0.32% impurity propylene subtracted

$F = (I_2)^{\frac{1}{2}} (C_3H_8)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity:- Runs 57 and 58 = 10^{-7} amp.

Runs 59 to 66 = 3×10^{-8} amp.

Peak Areas measured by integrator.

Plot for the determination of k_2:- Figure 20

Table IV.30 Iodine + Propane - 328.7°C (601.9°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(C_3H_8)x10^6$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area C_3H_8	Peak Area C_3H_6	Peak Area iPrI	Peak Area nPrI	Total Peak Area Products	% Products	(Products) $x10^8$ moles cc^{-1}
127	1.81	1.43	333	2.02	591	7.37	1.44	0.59	9.40	1.57	2.24
128	1.81	1.43	266	1.62	603	5.79	1.48	0.48	7.75	1.27	1.83
129	1.81	1.43	675	4.10	588	14.9	1.12	0.95	16.97	2.80	4.00
130	1.81	1.43	972	5.91	585	19.3	0.98	1.01	21.29	3.52	5.02
131	1.81	1.43	489	2.97	603	10.2	1.24	0.77	12.21	1.99	2.84
132	1.81	1.445	1205	7.40	584	24.3	0.90	0.99	26.19	4.28	6.18
133	1.81	1.44	1803	11.04	578	30.3	0.80	0.86	31.96	5.24	7.55
134	1.81	1.43	8608	52.32	557	52.4	0.69	0.235	53.3	8.73	12.5
135	1.81	1.44	612	3.75	601	13.15	1.29	0.95	15.39	2.50	3.60
136	1.81	1.44	2495	15.27	570	36.0	0.81	0.67	37.48	6.24	8.98
137	1.81	1.43	3067	18.64	535	32.0	0.675	0.535	33.21	5.84	8.40
138	1.81	1.44	4334	26.53	555	39.2	0.62	0.35	40.17	6.73	9.69
139	1.81	1.44	5171	31.65	566	42.0	0.69	0.29	42.98	7.05	10.2
140	1.81	1.44	7038	43.09	554	46.6	0.96	0.25	47.81	7.95	11.45
141	2.05	0.77	665	2.32	806	23.1	2.60	1.80	27.5	3.4	2.54
142	2.05	0.77	241	0.84	829	8.4	3.1	0.75	11.25	1.34	1.03
143	2.05	0.77	417	1.46	832	15.7	2.9	1.2	19.8	2.30	1.78

Table IV.30 continued on Page 85.

Table IV.30 Continued

Run	$(I_2) \times 10^7$ moles cc^{-1}	$(C_3H_8) \times 10^6$ moles cc^{-1}	Time(t) secs.	$F \times 10^7$	Peak Area C_3H_8	Peak Area C_3H_6	Peak Area iPrI	Peak Area nPrI	Total Peak Area Products	% Products	(Products) $\times 10^8$ moles cc^{-1}
144	2.05	0.77	1770	6.16	818	51.8	1.90	2.00	55.7	6.39	4.90
145	2.05	0.79	1061	3.78	801	36.3	2.30	2.00	40.6	4.84	3.80
146	2.05	0.77	2637	9.20	789	67.2	1.80	1.50	70.5	8.21	6.32
147	2.05	0.77	6291	21.80	743	111	2.20	0.74	113.9	13.3	10.2
148	2.05	0.78	3656	12.9	754	84.0	1.80	1.10	86.9	10.3	8.01
149	2.05	0.77	9625	33.35	777	124	3.30	0.61	127.9	14.1	10.8

$F = (I_2)^{\frac{1}{2}} (C_3H_8)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity:- Run 127 to 140 = 10^{-7} amp.

Run 141 to 149 = 3×10^{-7} amp.

Peak Areas measured by integrator.

Plot for the determination of k_2:- Figure 20

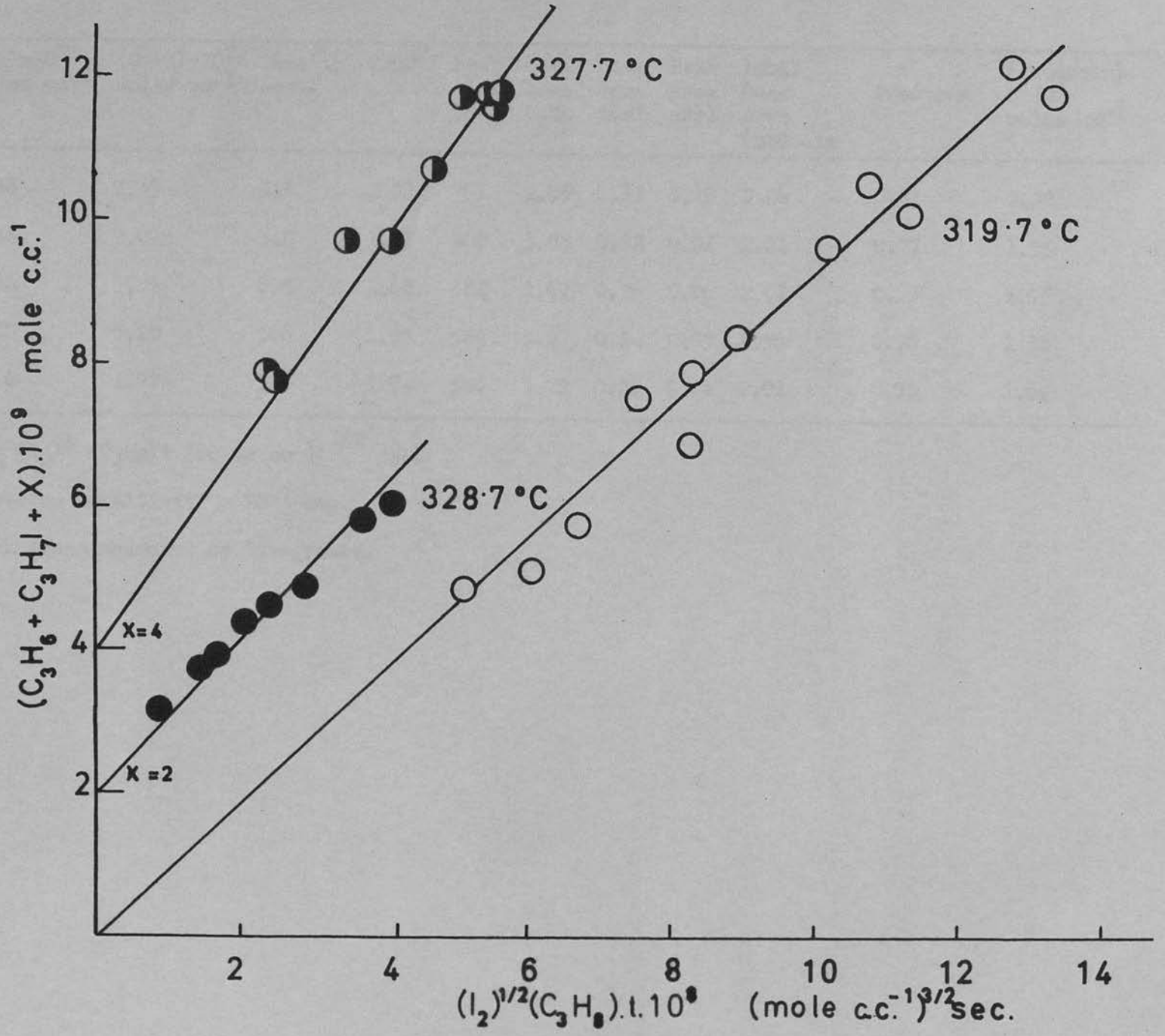


FIGURE-20 IODINE + PROPANE

Table IV.31 Iodination of Propane - 285.1°C (558.3°K)

- Reactions carried out in a packed vessel.

Run	$(I_2) \times 10^7$ moles cc^{-1}	$(C_3H_8) \times 10^7$ moles cc^{-1}	Time(t) secs.	$F \times 10^7$	Peak Area C_3H_8	Peak Area C_3H_6	Peak Area iPrI	Peak Area nPrI	Total Peak Area Products	% Products	(Products) x 10^9 moles cc^{-1}
150	2.58	7.35	545	2.03	791	2.05	0.31	0.10	2.46	0.31	2.28
151	2.58	7.095	340	1.23	800	1.88	0.32	0.04	2.24	0.27	1.95
152	2.10	5.31	690	1.68	584	1.69	0.26	0.06	2.01	0.33	1.75
153	2.10	5.20	566	1.35	589	1.27	0.24	0.05	1.56	0.26	1.36
154	2.10	4.97	765	1.74	586	1.72	0.23	0.06	2.01	0.33	1.64

$F = (I_2)^{\frac{1}{2}} (C_3H_8)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Table IV.32 Iodination of Propane - 310.7°C (583.9°K)

- Reactions carried out in a packed vessel.

Run	$(I_2) \times 10^7$ moles cc^{-1}	$(C_3H_8) \times 10^7$ moles cc^{-1}	Time(t) secs.	$F \times 10^7$	Peak Area C_3H_8	Peak Area C_3H_6	Peak Area iPrI	Peak Area nPrI	Total Peak Area Products	% Products	(Products) $\times 10^9$ moles cc^{-1}
155	2.22	7.72	446	1.62	758	7.10	1.96	0.33	9.39	1.22	9.38
156	2.22	7.28	473	1.62	773	7.95	1.65	0.44	9.04	1.16	8.44
157	2.005	5.85	608	1.59	462	5.50	1.61	0.33	7.44	1.56	9.12
158	2.005	6.15	592	1.63	466	6.11	1.48	0.31	7.90	1.64	10.08

$F = (I_2)^{\frac{1}{2}} (C_3H_8)t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Table IV.33

Iodine + Propane - Data for Arrhenius Plot

T°K	$\frac{1}{T°K} \times 10^3$	$k_2 \times 10^4$ cc/mole-sec.	$\log k_2$	$K_{I_2} \times 10^8$ $(moles/cc)^{\frac{1}{2}}$
601.9	1.661	19.1	5.28	57.0
600.9	1.664	26.9	5.43	55.0
592.9	1.687	20.4	5.31	45.2
592.5	1.688	14.7	5.17	45.0
579.9	1.724	10.0	5.00	32.3
572.1	1.749	10.6	5.025	26.2
568.0	1.761	6.60	4.82	23.3
558.9	1.789	5.60	4.75	18.4
554.0	1.805	4.56	4.66	15.7
553.4	1.807	3.85	4.585	15.5
544.5	1.836	2.32	4.365	12.0
558.3*	1.792	6.33	4.80	18.0
583.9*	1.715	16.2	5.21	36.0

* Reaction carried out in packed vessel.

Arrhenius Plot:- Figure 25

$\log k_2 = (14.39 \pm 0.4) - (24,800 \pm 1000)/2.303RT$

(c.c. $mole^{-1} sec.^{-1}$)

$\overline{IV}$.3 The Reaction of Iodine with Isobutane in the temperature range 226°C to 306.4°C

Tables $\overline{IV}$.34 to $\overline{IV}$.48 give the experimental details for the reaction of iodine with isobutane. The tables are listed in order of increasing temperature and the runs are numbered in the order in which they were carried out.

Table $\overline{IV}$.34

Isobutane + Iodine - 226.6°C (499.8°K)

Run	$(I_2)\times10^7$ moles cc^{-1}	$(iC_4H_{10})\times10^6$ moles cc^{-1}	Time(t) secs.	$F\times10^6$	Peak Area iC_4H_{10}	Peak Area iC_4H_{10}	% iC_4H_8	$(iC_4H_8)\times10^9$ moles cc^{-1}
140	2.79	1.90	1760	1.77	95.0	0.08	0.085	1.62
141	2.79	1.95	3760	3.87	98.4	0.15	0.15	2.90
142	2.79	1.95	5250	5.405	104.4	0.18	0.17	3.34
143	2.79	1.91	1775	1.79	99.6	0.07	0.07	1.30
144	3.69	1.56	1690	1.60	87.2	0.085	0.10	1.60
145	3.69	1.56	2625	2.49	82.2	0.11	0.13	2.00
146	3.69	1.53	1535	1.43	86.4	0.06	0.07	1.00

$F = (I_2)^{\frac{1}{2}} (iC_4H_{10})t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 3×10^{-7} amp.

Peak Areas measured by planimeter.

Plot for the determination of k_2:- Figure 21

Table IV.35

Isobutane + Iodine - 236.2°C (509.4°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(iC_4H_{10})x10^6$ moles cc^{-1}	Time(t) secs.	$Fx10^6$	Peak Area iC_4H_{10}	Peak Area iC_4H_8	% iC_4H_8	$(iC_4H_8)x10^9$ moles cc^{-1}
147	2.30	1.93	1765	1.635	98.4	0.11	0.113	2.18
148	2.83	1.91	3325	3.38	97.0	0.276	0.279	5.33
149	2.30	1.96	7295	6.86	100.6	0.575	0.569	11.1
150	2.30	1.94	2425	2.26	97.4	0.212	0.217	4.21
151	3.62	1.78	1235	1.32	101.0	0.084	0.084	1.49
152	3.62	1.76	904	0.93	84.4	0.083	0.098	1.73
153	3.62	1.78	2245	2.405	93.2	0.152	0.163	2.90
154	3.62	1.81	2220	2.42	90.0	0.181	0.200	3.60

$F = (I_2)^{\frac{1}{2}} (iC_4H_{10})t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 3×10^{-7} amp.

Peak Areas measured by planimeter.

Plot for the determination of k_2:- Figure 21

Table IV.36

Isobutane + Iodine - 248.3°C (521.5°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(iC_4H_{10})x10^6$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area iC_4H_{10}	Peak Area iC_4H_8	% iC_4H_8	$(iC_4H_8)x10^9$ moles cc^{-1}
70	3.14	1.07	450	2.70	1548	1.17	0.075	0.85
71	3.14	1.07	1246	7.47	1569	4.2	0.27	2.85
72	3.14	1.07	1057	6.33	1530	2.36	0.154	1.65
73	3.12	1.09	3975	24.3	1509	14.5	0.96	10.4
74	3.14	1.09	883	5.39	1509	3.3	0.22	2.4
75	3.14	1.09	885	5.40	1512	3.2	0.21	2.3
76	3.14	1.09	1747	10.7	1496	6.5	0.43	4.7
77	3.14	1.09	3022	18.4	1535	12.6	0.81	8.9
78	3.14	1.08	4575	27.7	1535	17.9	1.15	12.6
79	2.43	1.10	1450	7.86	1558	6.07	0.39	4.26
80	2.43	1.10	2564	13.9	1519	6.96	0.46	5.05
81	2.43	1.10	3964	21.5	1516	12.6	0.83	9.1
82	2.43	1.10	1904	10.3	1512	6.06	0.40	4.4
83	2.43	1.10	9980	54.1	1493	32.4	2.12	23.4
84	2.43	1.10	1811	9.81	1498	6.54	0.44	4.35
85	2.43	1.095	869	4.69	1496	3.02	0.20	2.20
86	3.97	0.63	2190	8.66	3165	26.0	0.82	5.12
87	3.97	0.62	4087	20.0	916	12.1	1.17	7.21
88	3.97	0.62	3105	12.0	914	8.8	0.95	5.8
89	2.97	0.62	1313	5.13	921	3.8	0.41	2.55

$F = (I_2)^{\frac{1}{2}} (iC_4H_{10})t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity:- Runs 70 to 85 and 87 to 89 = 10^{-7} amp.

Run 86 = 3×10^{-8} amp.

Plot for the determination of k_2:- Figure 21

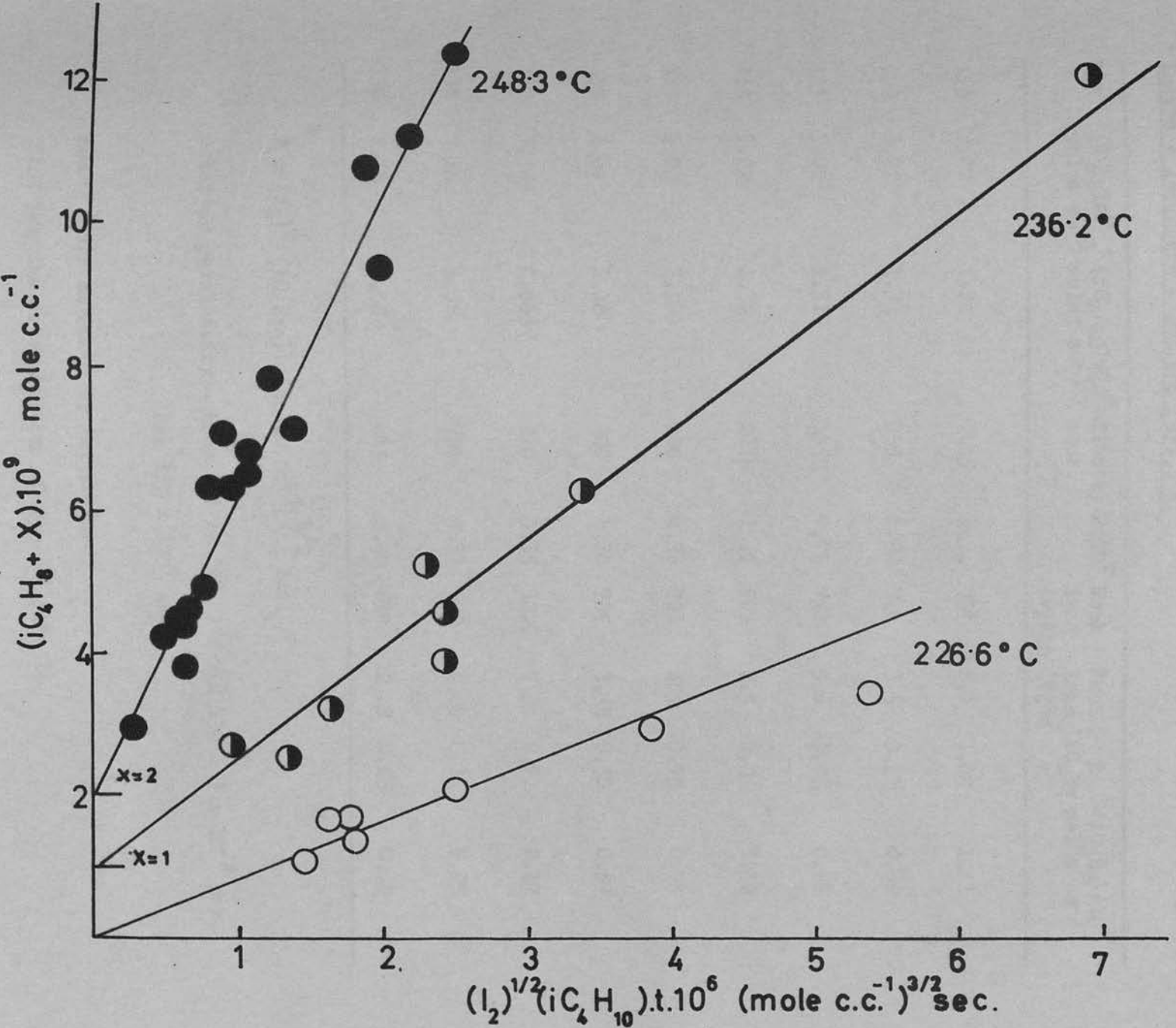


FIGURE-21 IODINE + ISOBUTANE

Table IV.37

Iodine + Isobutane - 264.0°C (537.2°K)

Run	$(I_2)\times10^7$ moles cc^{-1}	$(iC_4H_{10})\times10^6$ moles cc^{-1}	Time(t) secs.	$F\times10^7$	Peak Area iC_4H_{10}	Peak Area iC_4H_8	% iC_4H_8	$(iC_4H_8)\times10^8$ moles cc^{-1}
131	3.02	1.31	2015	14.4	739	8.1	1.08	1.41
132	3.02	1.31	955	6.88	740	3.5	0.47	0.62
133	3.02	1.31	1355	9.75	741	5.6	0.75	0.98
134	3.02	1.32	2115	15.3	702	8.5	1.2	1.58
135	3.02	1.29	900	6.38	701	405	0.58	0.75
136	4.69	1.18	780	6.30	705	3.55	0.50	0.59
137	3.585	0.665	840	3.35	1020	7.3	0.71	0.47
138	2.18	1.58	720	5.31	833	2.89	0.35	0.55
139	2.18	1.58	665	4.90	859	2.43	0.28	0.45

$F = (I_2)^{\frac{1}{2}} (iC_4H_{10})t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity:- Runs 131 to 136, 138 and 139 = 3×10^{-8} amp.

Run 137 = 10^{-7} amp.

Peak Areas measured by integrator.

Plot for the determination of k_2:- Figure 22

Table IV.38

Isobutane + Iodine - 277.3°C (550.5°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(iC_4H_{10})x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area iC_4H_{10}	Peak Area iC_4H_8	% iC_4H_8	$(iC_4H_8)x10^8$ moles cc^{-1}
56	2.46	6.88	644	2.20	983	6.33	0.64	0.40
57	2.46	6.88	2280	9.36	980	25.8	2.56	1.77
58	2.46	6.97	12019	41.6	870	85.6	8.97	6.25
59	2.46	6.91	352	1.21	994	5.32	0.54	0.37
60	2.46	6.91	2408	8.25	959	32.2	3.25	2.25
61	2.46	7.02	911	3.17	973	14.0	1.42	0.995
62	2.46	6.82	1314	4.45	976	17.7	1.80	1.24
63	2.46	7.02	1662	5.79	947	25.0	2.57	1.81
64	2.46	7.02	3251	11.3	925	42.2	4.35	3.06
65	2.46	6.79	4402	14.8	943	49.8	5.04	3.42
66	2.46	6.97	10895	37.65	863	96.5	10.5	7.00
67	2.46	6.82	7280	24.6	893	75.2	7.77	5.30
68	2.46	6.97	433	1.50	966	5.9	0.61	0.42
69	2.46	6.97	907	3.14	953	11.2	1.6	0.81

$F = (I_2)^{\frac{1}{2}} (iC_4H_{10})t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Plot for the determination of k_2:- Figure 22

Table IV.39

Isobutane + Iodine - 286.5°C (559.7°K)

Run	$(I_2)\times10^7$ moles cc^{-1}	$(iC_4H_{10})\times10^7$ moles cc^{-1}	Time(t) secs.	$F\times10^7$	Peak Area iC_4H_{10}	Peak Area iC_4H_8	% iC_4H_8	(iC_4H_8) $\times10^8$ moles cc^{-1}	I Ratio	P Ratio
48	2.50	7.74	308	1.19	I - P113.4	1.01	0.89	0.68		
49	2.50	7.91	673	2.66	I - P109.2	2.21	1.98	1.56		
50	2.50	7.97	914	3.64	I - P107.8	3.03	2.74	2.18		
51	2.50	7.77	1780	6.92	I1128 P110.4	50.1 4.82	4.26 4.18	3.31 3.25	1.79	1.77
52	2.50	7.77	2374	9.22	I1111 P104.0	65.4 6.39	5.58 5.78	4.34 4.49	2.38	2.41
53	2.50	7.94	2983	11.80	I1093 P105.2	69.6 6.78	5.99 6.05	4.76 4.82	0.767	0.776
54	2.50	7.91	3578	14.15	I1076 P103.4	85.7 8.34	7.37 7.46	5.84 5.91	0.96	0.97
55	2.50	7.91	5343	21.1	I1029 P99.4	109.9 10.62	9.64 9.66	7.62 7.63	1.29	1.29

I = integrator P = planimeter

Ratio = $\frac{\text{AiButene}}{\text{AiButane}}$

A = peak area uncorrected for different sensitivities.

$F = (I_2)^{\frac{1}{2}} (iC_4H_{10})t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Plot for the determination of k_2:- Figure 22

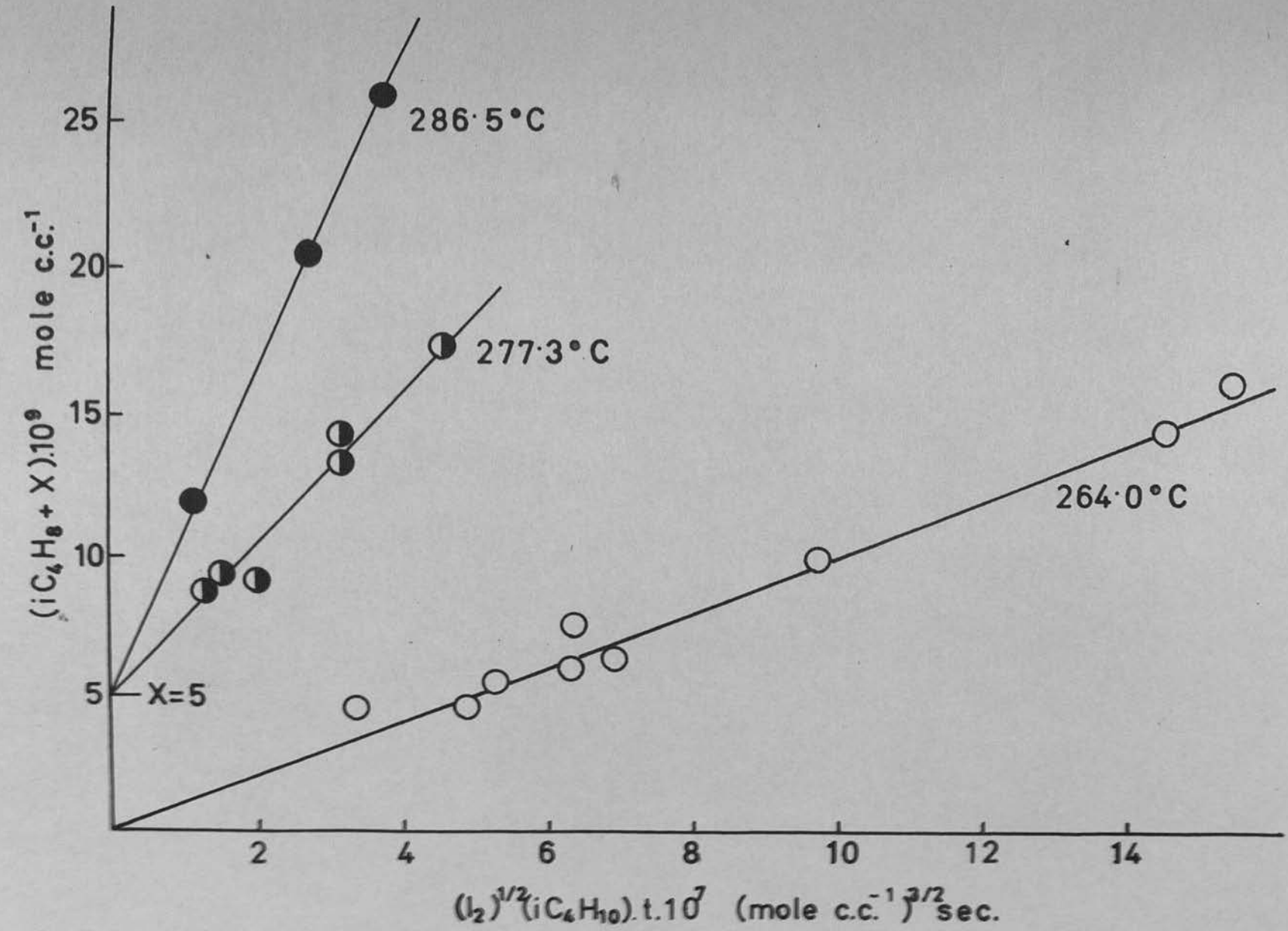


FIGURE-22 IODINE + ISOBUTANE

Table IV.40

Isobutane + Iodine - 294.3°C (567.5°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(iC_4H_{10})x10^6$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area iC_4H_{10}	Peak Area iC_4H_8	% iC_4H_8	$(iC_4H_8)x10^8$ moles cc^{-1}
100	2.06	1.06	480	2.31	1470	21.7	1.45	1.54
101	2.06	1.06	315	1.52	1488	14.7	0.98	1.04
102	2.06	1.07	310	1.51	1472	14.3	0.96	1.03
103	2.06	1.07	435	2.11	1435	19.9	1.37	1.47
104	2.06	1.09	260	1.29	1450	13.3	0.91	0.99
105	2.06	1.08	605	3.00	1424	28.4	1.95	2.11
106	2.06	1.076	615	3.00	1409	26.4	1.84	2.00
107	2.06	1.075	630	3.07	1439	26.7	1.82	1.95

$F = (I_2)^{\frac{1}{2}} (iC_4H_{10})t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Plot for the determination of k_2:- Figure 23

Table IV.41

Isobutane + Iodine - 295.7°C (568.9°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(iC_4H_{10})x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area iC_4H_{10}	Peak Area iC_4H_8	% iC_4H_8	$(iC_4H_8)x10^8$ moles cc^{-1}
37	2.06	5.22	615	1.46	235	4.75	1.98	1.04
38	2.06	5.28	7665	18.4	60.4	11.87	16.45	8.68
39	2.06	5.30	383	0.92	70.0	1.17	1.63	0.86
40	2.06	5.28	1197	2.87	69.6	3.32	4.55	2.41
41	2.06	5.22	871	2.06	67.5	2.40	3.44	1.79
42	2.06	5.22	3760	8.91	64.0	8.23	11.55	6.05
43	2.06	5.22	1760	4.17	70.0	4.92	6.57	3.43
44	2.06	5.14	2395	5.59	67.8	6.34	8.55	4.40
45	2.06	5.22	2950	6.99	68.0	7.50	10.1	5.24
46	2.06	5.22	9297	22.0	57.8	14.75	20.3	10.6
47	2.06	5.28	5165	12.4	59.6	10.85	15.5	8.20

$F = (I_2)^{\frac{1}{2}} (iC_4H_{10})t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity:- Run 37 = 3×10^{-8} amp.

Run 38 to 47 = 10^{-7} amp.

Peaks measured by planimeter.

Plot for the determination of k_2:- Figure 23

Table IV.42

Isobutane + Iodine - 296.7°C (569.9°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(iC_4H_{10})x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area iC_4H_{10}	Peak Area iC_4H_8	% iC_4H_8	$(iC_4H_8)x10^8$ moles cc^{-1}
24	1.27	3.8	1640	2.22	192.0	14.5	7.02	2.67
25	1.27	4.17	2186	3.24	209.2	23.4	10.05	4.20
26	1.27	4.105	12900	19.1	179.0	54.6	23.4	9.60
27	1.27	4.22	7260	10.9	174.8	40.8	18.9	7.96
28	1.27	4.13	498	0.73	208.6	5.85	2.73	1.13
29	1.27	4.17	1140	1.69	207.0	12.3	5.63	2.35
30	1.27	4.17	853	1.27	202.8	9.0	4.26	1.78
31	1.27	4.17	2105	3.12	192.4	18.9	8.95	3.73
32	1.27	4.17	20500	30.4	170.4	55.6	24.6	10.25
33	1.27	4.17	3360	4.98	192.6	27.1	12.35	5.14
34	1.27	4.155	320	0.47	205.2	3.49	1.67	0.69
35	1.27	4.17	853	1.27	187.8	5.91	3.05	1.27
36	3.10	1.97	2041	2.24	166.8	17.0	9.25	1.81

$F = (I_2)^{\frac{1}{2}} (iC_4H_{10})t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 3×10^{-8} amp.

Peak Area measured by planimeter.

Plot for the determination of k_2:- Figure 23

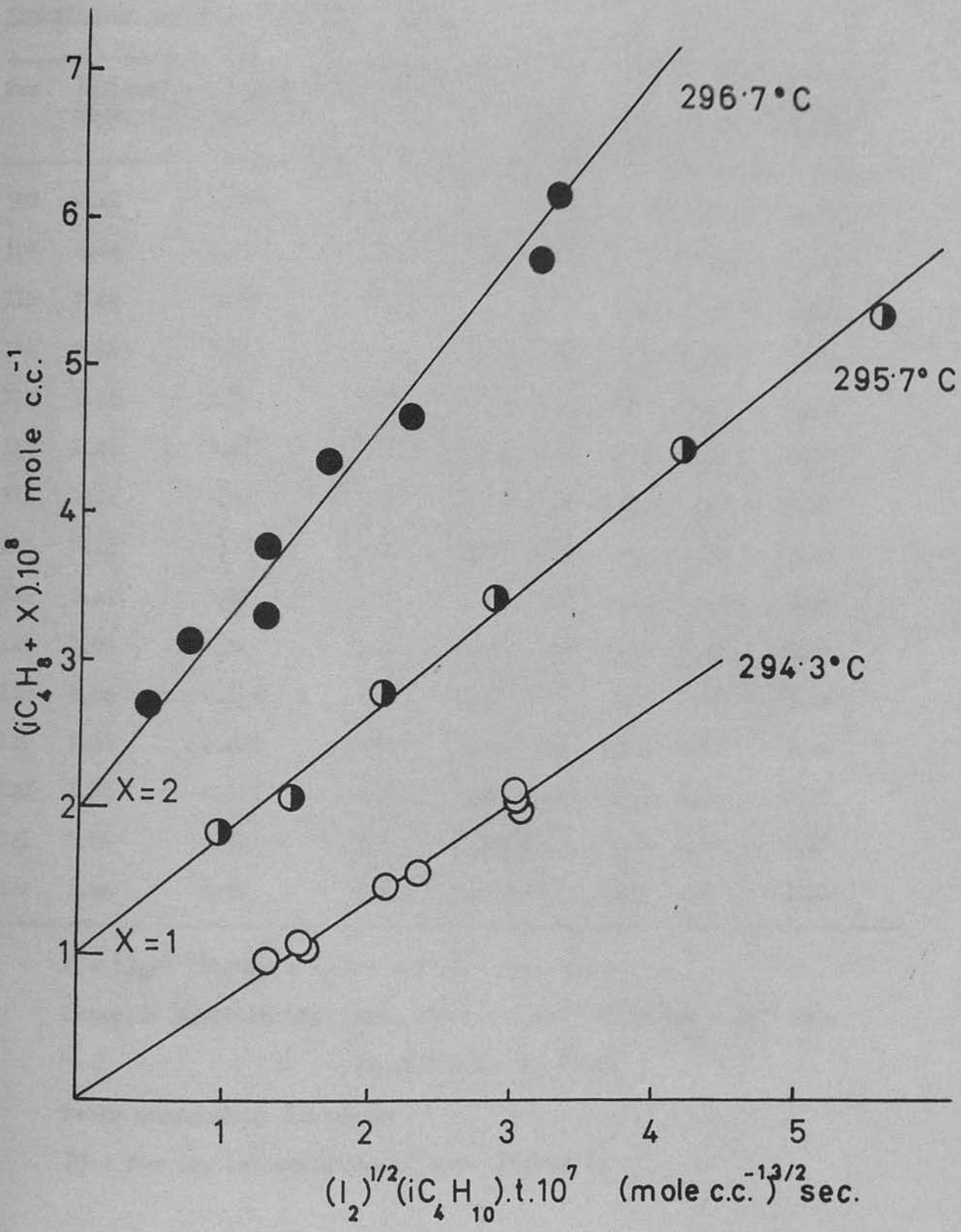


FIGURE-23 IODINE + ISOBUTANE

Table IV.43

Isobutane + Iodine - 298.8°C (572.0°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(iC_4H_{10})x10^6$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area iC_4H_{10}	Peak Area iC_4H_8	% iC_4H_8	$(iC_4H_8)x10^8$ moles cc^{-1}
108	2.44	1.03	600	3.05	1442	32.8	2.23	2.30
109	2.44	1.07	615	3.25	1426	37.5	2.56	2.74
110	2.44	1.08	860	4.59	1383	47.8	3.35	3.61
111	2.44	1.08	750	4.00	1401	47.7	3.29	3.55
112	2.44	1.08	900	4.80	1410	55.5	3.79	4.08
113	2.44	1.09	580	3.12	1426	40.0	2.74	2.98
114	2.44	1.09	317	1.71	1425	23.3	1.61	1.75
115	2.44	1.08	480	2.56	1435	33.1	2.26	2.44
116	2.44	1.09	210	1.13	1467	18.4	1.24	1.35
117	1.66	0.544	645	1.43	2327	60.3	2.53	1.38
118	1.66	0.578	630	1.48	692	21.5	3.01	1.74
119	1.66	0.581	455	1.08	708	18.5	2.56	1.48
120	1.66	0.584	445	1.06	701	19.4	2.70	1.57
121	1.66	0.559	310	0.705	714	14.4	1.97	1.10
122	1.66	0.57	350	0.812	709	16.7	2.3	1.31

$F = (I_2)^{\frac{1}{2}} (iC_4H_{10})t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity:- Runs 108 - 116 and 118 to 122 = 10^{-7} amp.

Run 117 = 3×10^{-8} amp.

Peaks measured by Integrator.

Plot for the determination of k_2:- Figure 24

Table IV.44

Isobutane + Iodine - 300°C (573.2°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(iC_4H_{10})x10^6$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area iC_4H_{10}	Peak Area iC_4H_8	% iC_4H_8	$(iC_4H_8)x10^8$ moles cc^{-1}
90	2.85	1.03	480	2.64	1475	51.6	3.38	3.48
91	2.85	1.06	770	4.36	1428	95.7	6.29	6.66
92	2.85	1.04	1020	5.66	1416	107.2	7.04	7.32
93	2.85	1.05	377	2.11	1270	47.9	3.64	3.82
94	2.85	1.04	300	1.665	1386	41.2	2.92	3.04
95	2.04	1.06	510	2.44	1502	54.7	3.53	3.74
96	2.04	1.06	255	1.25	1539	34.6	2.2	2.33
97	2.04	1.07	450	2.18	1529	62.7	3.93	4.2
98	2.04	1.07	540	2.61	1510	71.2	4.50	4.82
99	2.04	1.06	1050	5.03	1464	107.5	6.85	7.46

$F = (I_2)^{\frac{1}{2}} (iC_4H_{10})t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Plot for the determination of k_2:- Figure 24

Table IV.45

Isobutane + Iodine - 306°C (579.2°K)

Run	$(I_2)x10^7$ moles cc^{-1}	$(iC_4H_{10})x10^6$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area iC_4H_{10}	Peak Area iC_4H_8	% iC_4H_8	$(iC_4H_8)x10^8$ moles cc^{-1}
123	2.08	1.075	390	1.91	1487	53.5	3.48	3.74
124	2.08	1.05	225	1.08	1502	32.9	2.14	2.25
125	2.08	1.07	330	1.61	1519	41.0	2.63	2.81
126	2.08	1.055	315	1.52	1518	40.5	2.63	2.77
127	2.08	1.10	305	1.53	1476	41.7	2.76	3.03
128	2.08	1.07	255	1.24	1536	36.2	2.30	2.46
129	2.08	1.11	225	1.14	1479	33.5	2.21	2.45
130	2.08	1.09	430	2.14	1467	57.0	3.72	4.08

$F = (I_2)^{\frac{1}{2}} (iC_4H_{10})t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 10^{-7} amp.

Peak Areas measured by integrator.

Plot for the determination of k_2:- Figure 24

Table IV.46

Isobutane + Iodine - 306.4°C (579.6°K)

Run	$(I_2)x10^8$ moles cc^{-1}	$(iC_4H_{10})x10^7$ moles cc^{-1}	Time(t) Secs.	$Fx10^7$	Peak Area iC_4H_{10}	Peak Area iC_4H_8	% iC_4H_8	$(iC_4H_8)x10^8$ moles cc^{-1}
1	9.69	2.63	632	0.517	100.4	5.27	4.99	1.38
2	9.69	2.49	343	0.266	120.8	3.12	2.54	0.63
3	9.69	2.63	574	0.469	119.7	5.28	4.23	1.12
4	9.69	2.63	2273	1.86	112.8	19.8	14.9	3.93
5	9.69	2.63	1020	0.84	125.8	10.65	7.85	2.07
6	9.69	2.58	1384	1.11	122.6	12.1	9.4	2.42
7	9.69	2.63	2703	2.21	114.6	21.3	16.35	4.30
8	9.97	2.69	3506	2.89	109.0	25.3	18.80	5.06
9	9.69	2.63	439	0.36	122.2	5.97	4.65	1.22
10	9.69	2.63	12892	10.5	90.4	34.9	27.10	7.10
11	9.69	2.66	866	0.72	122.2	9.50	7.20	1.92
12	9.69	2.66	2129	1.76	114.4	16.30	12.4	3.31
13	9.69	2.58	5234	4.20	100.8	27.6	21.5	5.55
14	20.2	5.43	898	2.19	242.2	25.9	9.67	5.25
15	20.2	5.32	594	1.42	279.6	21.3	7.10	3.77
16	20.2	5.43	400	0.98	278.6	13.85	4.73	2.56
17	20.2	5.32	172	0.41	254.8	4.72	1.82	0.97
18	20.2	5.29	18067	42.9	204.0	75.2	21.0	11.10
19	20.2	5.32	261	0.62	269.8	10.25	3.66	1.92
20	20.2	5.32	2363	5.64	219.8	35.5	13.90	7.40
21	20.2	5.32	5401	12.9	210.4	60.2	22.1	11.8

Table IV.46 Continued on Page 102.

Table IV.46 (Continued)

Run	$(I_2)x10^8$ moles cc^{-1}	$(iC_4H_{10})x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^7$	Peak Area iC_4H_{10}	Peak Area iC_4H_8	% iC_4H_8	$(iC_4H_8)x10^8$ moles cc^{-1}
22	13.3	2.52	419	0.385	122.2	5.86	4.57	1.15
23	9.69	2.56	3294	2.62	106.3	30.5	22.3	5.7

$F = (I_2)^{\frac{1}{2}} (iC_4H_{10})t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity = 3×10^{-8} amp.

Peak Areas measured by planimeter.

Plot for the determination of k_2:- Figure 24

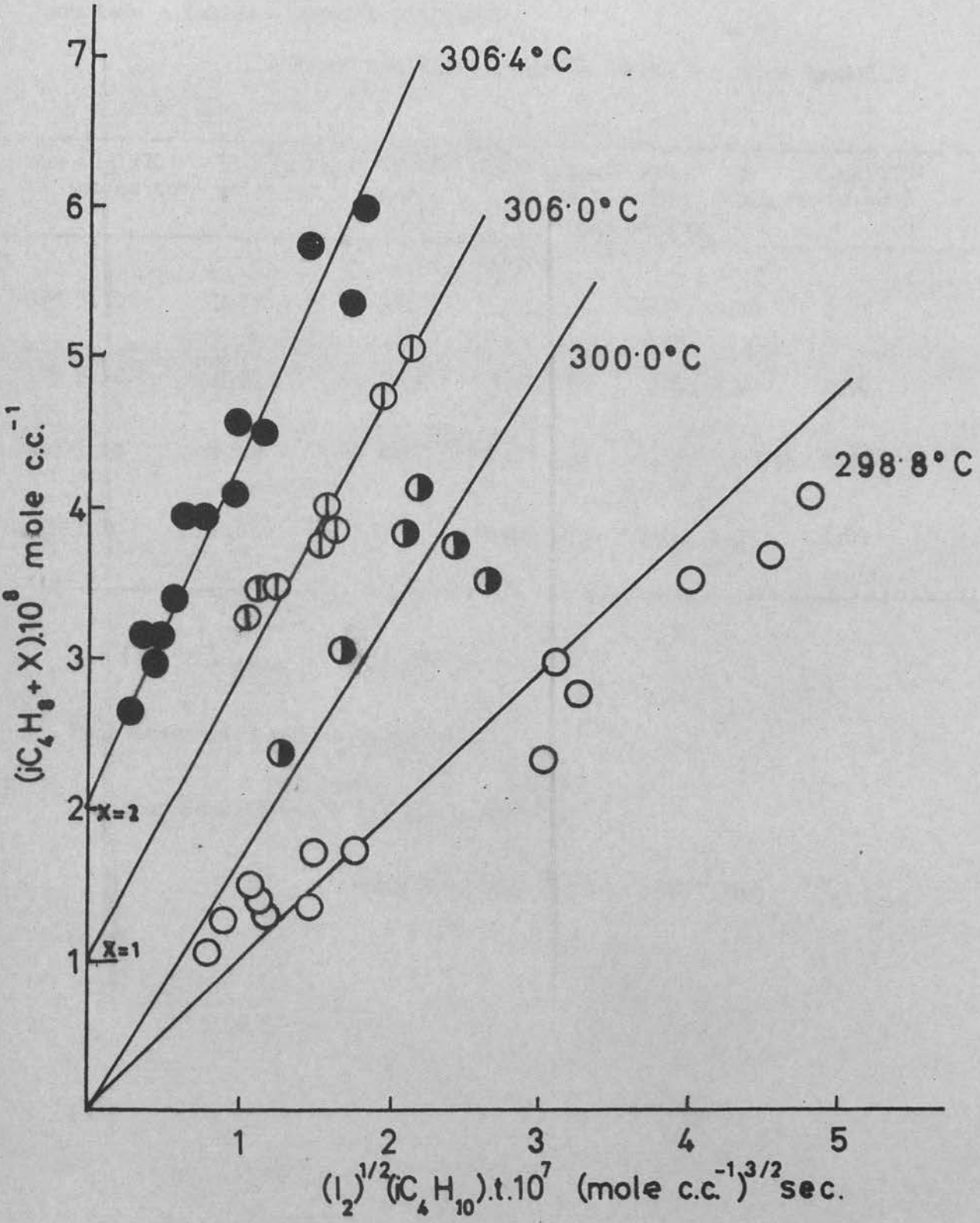


FIGURE-24 IODINE + ISOBUTANE

Table IV.47

Isobutane + Iodine - 249.0°C (522.2°K)

- Reactions carried out in packed reaction vessel.

Run	$(I_2)x10^7$ moles cc^{-1}	$(iC_4H_{10})x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^8$	Peak Area iC_4H_{10}	Peak Area iC_4H_8	% iC_4H_8	$(iC_4H_8)x10^9$ moles cc^{-1}
155	3.10	3.57	701	33.46	414	0.70	0.17	1.45
156	3.10	8.81	1140	55.94	1239	3.62	0.29	2.56
157	3.10	8.88	897	44.37	1229	2.54	0.206	1.83
158	3.10	8.57	768	36.66	1290	2.46	0.19	1.63

$F = (I_2)^{\frac{1}{2}} (iC_4H_{10})t$ (moles $cc^{-1})^{3/2}$ sec.

Peak Areas measured by integrator.

Detector Sensitivity:- Run 155 = 10^{-7} amp.

Runs 156, 157, 158 = 3×10^{-8} amp.

Table IV.48

Isobutane + Iodine - 271.8°C (545.0°K)

- Reactions carried out in packed reaction vessel.

Run	$(I_2)x10^7$ moles cc^{-1}	$(iC_4H_{10})x10^7$ moles cc^{-1}	Time(t) secs.	$Fx10^8$	Peak Area iC_4H_{10}	Peak Area iC_4H_8	% iC_4H_8	$(iC_4H_8)x10^9$ moles cc^{-1}
159	2.68	8.30	606	26.05	1255	10.59	0.83	6.91
160	2.68	8.24	441	18.82	1320	8.50	0.64	5.27
161	2.29	6.03	488	14.06	936	5.00	0.53	3.21
162	2.29	6.47	489	15.12	926	5.01	0.54	3.48
163	2.29	5.62	384	10.32	944	3.92	0.41	2.33

$F = (I_2)^{\frac{1}{2}} (iC_4H_{10})t$ (moles $cc^{-1})^{3/2}$ sec.

Detector sensitivity:- 3×10^{-8} amp.

Peak Areas measured by integrator.

Table IV.49

Iodine + Isobutane - Data for Arrhenius Plot

$T^{o}K$	$\frac{1}{T^{o}K} \times 10^{3}$	$k \times 10^{-4}$ cc $mole^{-1} sec.^{-1}$	logk	$K_{I_2} \times 10^{8}$ $(moles\ cc)^{\frac{1}{2}}$
579.6	1.725	79.6	5.901	32.50
579.2	1.726	62.3	5.794	32.0
573.2	1.745	63.0	5.799	27.40
572.0	1.478	39.0	5.591	25.64
569.9	1.755	52.9	5.723	25.10
568.9	1.758	35.1	5.545	23.9
567.5	1.762	29.1	5.464	23.6
559.7	1.787	31.3	5.495	18.8
550.5	1.816	18.6	5.269	14.5
537.2	1.861	10.95	5.039	9.50
521.5	1.917	7.70	4.886	5.70
509.4	1.963	3.93	4.594	3.84
499.8	2.001	2.94	4.468	2.68
522.2*	1.915	8.70	4.94	5.70
545.0*	1.839	20.3	5.31	12.2

* Reaction carried out in packed vessel. Arrhenius Plot:- Figure 25

$\log k_2 = (13.96 \pm 0.31) - 21,800 \pm 800/2.303RT$

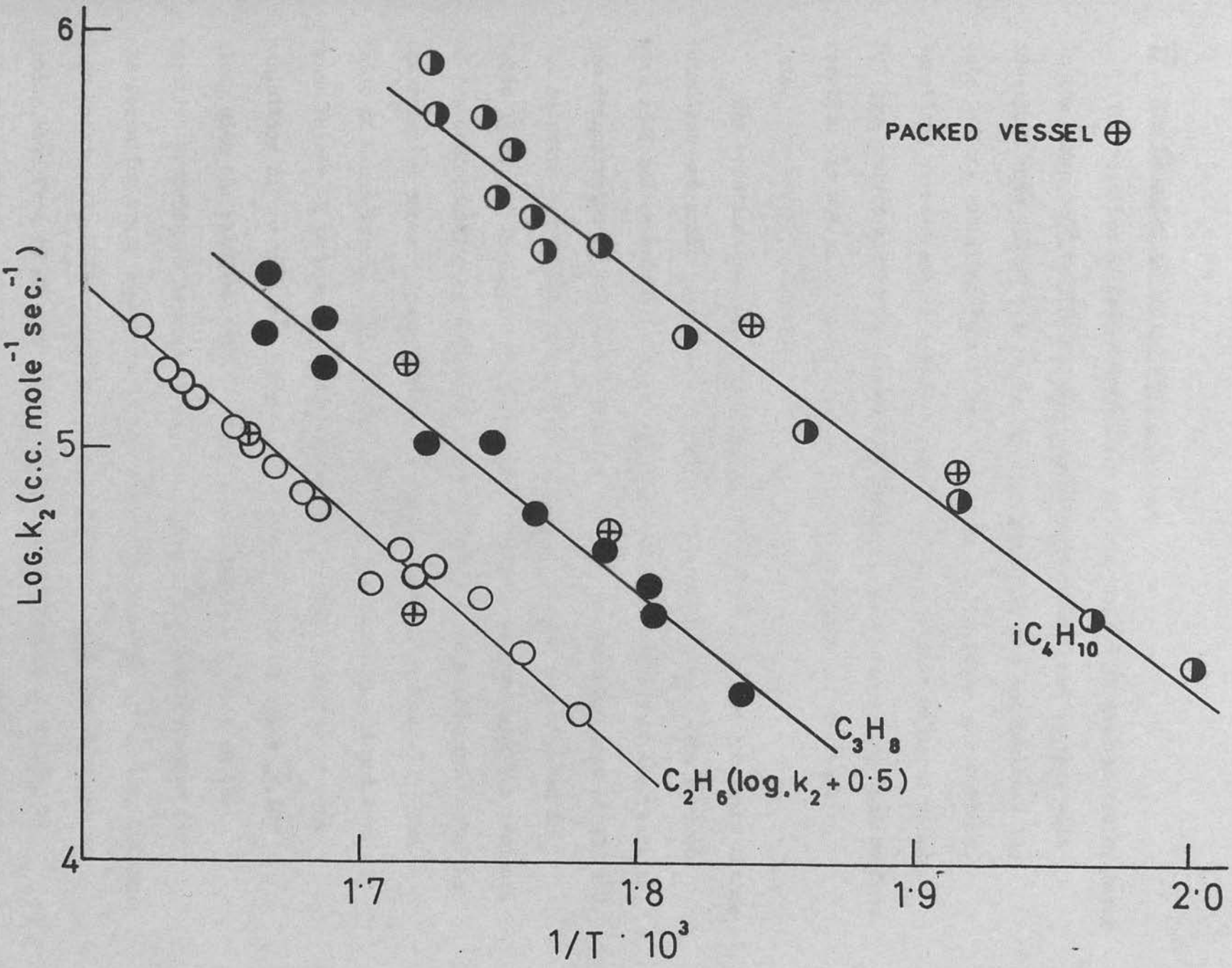


FIGURE-25 ARRHENIUS PLOT FOR k_2

IV.4 The Reaction of Iodine with n-Butane

The reaction of iodine with n-butane was studied at several temperatures in the range 280° to 300°C. The reaction rate was found to vary with identical runs and as the source of this variation was not detected the data was not submitted to the same treatment as the other hydrocarbons. Reactions carried out in a packed vessel did not exhibit enhanced rates but gave values within the previously measured range suggesting that surface reaction was not an important factor in the variation of the reaction rate.

The reaction products were found to be butene - 1, cis and trans butene -2, butadiene and small quantities of secondary butyl iodide. The products were analysed on column 4 (Table III.1). Characteristics of the reaction are demonstrated by the data listed in Table IV.50 for reactions at 287.3°C. The relative quantities of the different products are demonstrated in Table IV.51 and in figure 26. The isomeric butenes represent the products of the decomposition of secondary butyl iodide and were always detected in the relative amounts trans butene - 2 > cis butene -2 > butene -1. The ratio of trans to cis butene -2 for all runs was close to 1.5 and that of trans butene -2 to butene -1 was generally 2.50 with a number of runs exhibiting higher values. These ratios are included in Table IV.50 along with the reaction data. Butadiene increases rapidly as the reaction proceeds as is demonstrated in figure 26. The mechanism for its formation would appear to be via the abstraction of a secondary hydrogen from butene -1. The resulting allylic radical could then abstract an iodine atom from I_2 and the decomposition of the resulting iodide, by elimination of HI, would lead to butadiene. Using the values for the Arrhenius parameters for the abstraction from butene -1 determined by Benson and his co-workers[63] the rate constant for the removal of butene -1 may/

/may be estimated. The A factor and activation energy have the respective values 10^{14} cc $mole^{-1}$ sec^{-1} and 24 kcal $mole^{-1}$ and the rate constant at 600°K is calculated to be 4.3×10^{7} cc $mole^{-1}$ $sec.^{-1}$. If the Arrhenius parameters for iodine atom abstraction from the secondary position in n-butane are assumed to be the same as those for propane, with a factor of 2 included in the A factor to allow for the greater number of secondary hydrogen atoms, the rate constant at 600°K can be taken as approximately 6×10^{4} cc $mole^{-1}$ $sec.^{-1}$. The rate constant for iodine atom attack on butene -1 is approximately 700 times greater than that for n-butane. The stationary state concentration of isomeric butenes, on the basis of these rate constant values, would be expected to be very low and the rate of formation of butadiene rapid. Both these predictions are confirmed by the experimental results.

Table IV.50:- Iodine + n-butane:- 287.20C (560.59K).

Run	$(I_2)x10^7$ moles cc^{-1}	$(nC_4H_{10})x10^7$ moles cc^{-1}	Time(t) secs.	Peak Area nC_4H_{10}	Peak Area Bu 1	Peak Area Bu C	Peak Area Bu T	Peak Area Bu D	Peak Area Bu2I	Bu T / Bu C	Bu T / Bu 1
1.	2.00	7.75	1408	1140	4.05	7.78	10.79	11.15	0.71	1.39	2.66
2	2.00	7.78	728	1145	3.09	5.34	7.50	6.42	0.60	1.40	2.42
3	2.00	7.78	1143	1187	3.79	6.87	9.24	11.34	0.65	1.34	2.44
4	2.00	7.81	368	1176	3.60	5.83	7.74	4.24	0.85	1.33	2.15
5	2.00	7.80	374	1172	2.91	5.47	7.29	4.60	0.89	1.33	2.50
6	2.00	7.87	1888	1147	5.55	9.29	13.88	18.70	0.64	1.49	2.50
7	1.54	5.41	453	836	1.77	3.96	5.13	5.84	0.56	1.30	2.90
8	1.54	5.55	863	853	1.17	4.39	5.83	6.38	0.54	1.33	4.98
9	1.54	5.55	5.46	853	1.72	3.88	5.32	4.01	0.69	1.37	3.09
10	1.54	5.55	353	853	1.98	330	4.62	2.40	0.60	1.40	2.33
11	1.54	5.58	366	870	2.12	3.90	562	2.54	0.62	1.44	2.65
12	1.54	5.58	873	873	1.73	4.47	6.08	6.52	0.62	1.36	3.5

Bu 1 = 1-butene Bu C = cis-butene-2 Bu T = trans butene-2 Bu D = butadiene

Detector Sensitivity = 10^{-7} amp. Peak Areas measured by integrator.

Table IV.51:- Relative quantities of products from the reaction of Iodine with n-Butane at 287.3°C

Run	% Reaction	% of Compound in Products Bu 1	Bu C	Bu T	Bu D	Bu2I
1	2.93	11.75	22.6	31.3	32.4	2.1
2	1.97	13.5	23.3	32.7	28.0	2.6
3	2.62	11.9	21.5	29.0	35.6	2.0
4	1.86	16.2	26.2	34.8	19.0	3.8
5	1.69	14.5	27.1	36.2	22.8	4.4
6	4.02	11.5	19.3	28.9	38.9	1.3
7	2.01	10.2	22.9	29.7	33.8	3.2
8	2.10	6.4	24.0	31.8	34.8	2.9
9	1.80	11.0	24.8	34.0	25.7	4.4
10	1.49	15.3	25.6	35.8	18.6	4.6
11	1.67	14.3	26.4	38.0	17.2	4.18
12	2.18	8.9	23.0	31.3	33.6	3.19

Bu 1 = butene-1, Bu C = cis-butene-2, BuT = trans-butene-2

Bu D = butadiene, Bu2I = sec-butyl iodide

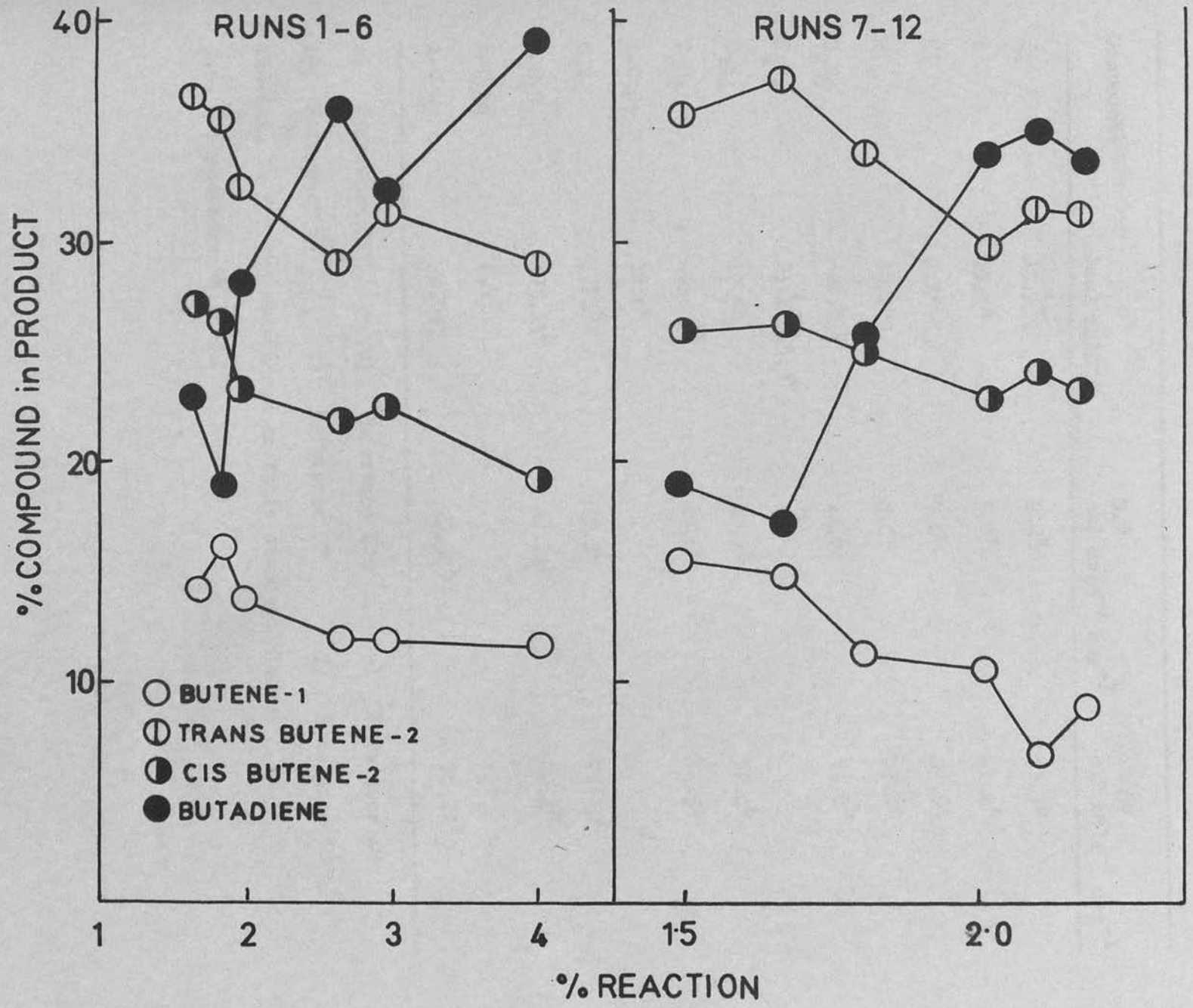


FIGURE-26 IODINE + n-BUTANE

Table V.1:- Thermodynamic Data

Compounds	H_f^o kcal mole^{-1}	C_p^o cal mole^{-1} deg^{-1}	S^o cal mole^{-1} deg^{-1}
I_2	14.9[a]	8.8[a]	62.3[a]
I	25.5[a]	5.0[a]	43.2[a]
HI	6.2[a]	7.0[a]	49.3[a]
H	52.1[a]	5.0[a]	27.4[a]
C_2H_6	-20.24[b]	12.6[b]	54.8[b]
C_2H_5	25.2[c], 25.3[d]		
C_2H_4	12.5[b]	10.4[b]	52.4[b]
C_3H_8	-24.82[b]	17.6[b]	64.5[b]
i-C_3H_7	17.6[e]		
C_3H_6	4.88[b]	15.3[b]	63.80[b]
i-C_4H_{10}	-32.15[b]	23.14[b]	70.4[b]
t-C_4H_9	6.7[f]		
i-C_4H_8	-4.04[b]	21.30[b]	70.17[b]

a) Reference 117 c) Reference 114 e) Reference 48

b) Reference 67 d) Reference 97 f) Reference 50

The data is for the substances in their standard states

i.e. 1 atmosphere at 25°C.

CHAPTER V

DISCUSSION

V.1 Arrhenius Parameters for Iodine atom abstraction reactions

As predicted by the theoretical consideration of the atomic chain mechanism for the reaction of iodine with hydrocarbons the graphs of products, i.e. olefine + iodide, against the function $[(I_2)^{\frac{1}{2}}(RH).time]$ are linear for the initial stages of the reaction and the gradients of these lines have yielded values for the rate constants of the reaction;

$$I + RH \longrightarrow R + HI \qquad 2.$$

The values obtained for k_2 for the reaction of iodine with isobutane are 5 to 10% below those determined by Benson and Teranishi[50]. The reaction of iodine with propane has yielded values of k_2 in excellent agreement with those reported by Benson and Nangia[47]. The values derived for the Arrhenius parameters are summarised in Table V.2 along with Benson's results. The agreement between the results obtained from the present work and those of Benson et al. is very good. The value of 26.3 kcal.mole^{-1} found for the activation energy of reaction 2 with ethane is 1.6 kcal.mole^{-1} less than that estimated by Benson and Hartley[97] from the results of their study of the reaction of hydrogen iodide with ethyl iodide.

Table V.2 - Arrhenius Parameters for Reaction 2.

Hydrocarbon	Activation Energy		log A factor	
	This work	Benson	This work	Benson
Ethane	26.3 ± 0.9		14.23 ± 0.4	
Propane	24.8 ± 1.0	25.5 ± 1.0	14.39 ± 0.4	14.53 ± 0.4
	24.6*		14.26*	
Isobutane	21.8 ± 0.8	21.4 ± 0.5	13.96 ± 0.31	13.88 ± 0.15
	21.56*		13.88*	

* Values/

/†Values corrected to allow for abstraction of hydrogen from primary position. Activation energies in kcal.mole^{-1} units, log (A factor) in log mole^{-1} cc sec.$^{-1}$ units. The errors quoted are the probable errors (0.67 σ).

In discussing the aim of this work, reference was made to the specific nature of the iodine atom attack on hydrocarbons, i.e. the abstraction of the hydrogen atom or atoms whose C-H bond dissociation energies were lowest. This specific attack would be of value in the evaluation of bond dissociation energies in hydrocarbons. It is necessary however to make allowance for the abstraction of hydrogen atoms other than those with the weakest bond. This may be done by making the assumption that the rate constant for the abstraction of a primary hydrogen atom is the same for ethane, propane and isobutane. The following relationships can then be written.

k° (Ethane) $= 6k_p$ - 1

k° (Propane) $= 6k_p + 2k_s$ - 2

k° (i-butane) $= 9k_p + kt$ - 3

Here k° is the measured rate constant, k_p is the rate constant for primary attack, k_s is that for secondary abstraction and k_t that for tertiary abstraction. The value of k_p can be calculated, at any temperature, by dividing the value of k° (Ethane), read from the least squares line of the Arrhenius plot for k° (Ethane), by six. The values of k_t and $2k_s$ can then be estimated from relationships 2 and 3, by using this value of k_p and values of k° (i-butane) and k° (propane) obtained in the same manner as k°(Ethane). The values for the activation energies and A factors for tertiary and secondary abstraction can be estimated from the values of k_t and $2k_s$ if these are known at two temperatures.

The/

/The calculations have been carried out at 500° and 600°K and the values found for k_p were respectively 0.66×10^2 and 4.4×10^3 $moles^{-1}cc.\ sec^{-1}$ and these in turn led to values for k_t of 2.77×10^4 and 1.03×10^6 $moles^{-1}cc.\ sec^{-1}$ and for $2k_s$ of 3.15×10^3 and 1.98×10^5 $moles^{-1}cc.\ sec^{-1}$. The activation energy and A factor for tertiary abstraction were then corrected to be 21.56 kcal $mole^{-1}$ and 13.88 $mole^{-1}cc.\ sec^{-1}$. These parameters for secondary abstraction from propane were found to be 24.6 kcal $mole^{-1}$ and 14.26 $mole^{-1}$ cc. sec^{-1}.

V.2 Estimation of C-H Bond Dissociation Energies

For reactions 2 and 4, i.e. $I + RH \underset{4}{\overset{2}{\rightleftharpoons}} R + HI$, the following expression holds.

$$D^\circ(R\text{-}H) - D^\circ(H\text{-}I) = \Delta H_{2.4}^\circ$$

Here $D^\circ(R\text{-}H)$ and $D^\circ(H\text{-}I)$ represent the bond dissociation energies for the substances and $\Delta H^\circ_{2.4}$ represents the heat of reaction, the substances being in the standard state. The value of $\Delta H_{2.4}$ may be calculated from the expression:

$$E_2 - E_4 = \Delta H_{2.4}$$

where E_2 and E_4 are the activation energies of the reactions 2 and 4. The values of E_2 for ethane, the secondary positions in propane and the tertiary position in isobutane have been determined in the present work and the value of $D^\circ(H\text{-}I)$, (25°C), is well established as 71.4 kcal/mole[105,106]. In order to calculate $\Delta H_{2.4}$ the values of E_4 remain to be estimated.

Hartley and Benson[97] obtained the difference $E_4 - E_3$ for the ethyl radical to be 0.9 $kcal.mole^{-1}$ where reaction 3 was $R + I_2 \longrightarrow RI + I$. Teranishi and Benson[50] obtained 1.4 $kcal.mole^{-1}$ for this difference for the reactions of a t-butyl radical. It would appear reasonable to assume $E_3 = 0$ and assign values of 0.9 and 1.4 kcal $mole^{-1}$ to E_4 for the ethyl and/

/and t-butyl radicals respectively. A reasonable value of E_4 for the isopropyl radical would then be 1.2 kcal.mole^{-1}

The values of $\triangle H_{2.4}$ resulting from these estimated values of E_4, and the corrected experimental values of E_2, are given in Table $\bar{V}$.3 below. Using the thermodynamic data in Table $\bar{V}$.1, assuming that C_p° for the radicals is equal to that for the parent hydrocarbon and that $\triangle C_p^\circ$ for the reactions remained constant with temperature, the values of $\triangle H_{2.4}$ were corrected from the mean reaction temperature to $\triangle H_{2.4}$ (25°C) by the following relationship (Kirchhoff's Law).

$$\triangle H_{T_2} - \triangle H_{T_1} = \int_{T_1}^{T_2} \triangle C_p dT$$

The values of $\triangle H^\circ_{2.4}$ (25°C) are tabulated in Table $\bar{V}$.3 along with the values calculated for the R-H bond dissociation energies D°(R-H) at 25°C. Allowing for the errors in E_2 ($\sim \pm$ 1kcal mole^{-1}) and the estimated value of E_4 ($\pm$ 0.3 kcal mole^{-1}), and a small error introduced in the above calculation, a reasonable estimate for the maximum uncertainty in the bond dissociation energies would appear to be $\pm$ 1.5 kcal.mole^{-1}.

Table $\bar{V}$.3:- (R-H) bond dissociation energies and related data.

Radical R	E_2 kcal mole^{-1}	E_4 kcal mole^{-1}	Mean Reaction Temperature	$\triangle H_{2.4}$ kcal mole^{-1}	$\triangle H^\circ_{2.4}$ (25°C) kcal mole^{-1}	D°(R-H) kcal mole^{-1}
Ethyl	26.3	0.9	610°K	25.4	25.0	96.4
i-Propyl	24.6	1.2	600°K	23.4	22.8	94.2
t-Butyl	21.6	1.4	580°K	20.2	19.7	91.1

The value for the C-H bond in ethane of 96.4 kcal mole^{-1} is in excellent agreement with the 96* kcal mole^{-1} assessed by Cottrell[107] from a consideration of the results of electron impact and kinetic studies. The value of 94.2 kcal mole^{-1} obtained for the bond dissociation energy of a secondary hydrogen in propane agrees with the 94 $\pm$ 2 k cal mole^{-1} obtained by electron impact methods,/

* at 0°K

/methods,[108] and lies between the 93.1 kcal mole^{-1} obtained by Fettis and Trotman-Dickenson[109] from bromination studies and the 94.5 kcal mole^{-1} reported by Benson and Nangia[47] from their data on the iodination of propane. The dissociation energy of 91.1 kcal mole^{-1} found for the tertiary hydrogen bond in isobutane is in excellent agreement with the 90.9 kcal mole^{-1} reported by Benson and Teranishi[50], from iodination data, and a little above the bromination result[109] which was 90.0 kcal mole^{-1}. The electron impact value, reported by Stevenson[110] to be 89 ± 2 kcal mole^{-1}, appears to be slightly low.

V̄.3 Heats of Formation of Radicals

The heat of formation of a hydrocarbon radical may be determined from the following relationship.

$$\Delta H_f^\circ(R) = \Delta H_f^\circ(RH) - \Delta H_f^\circ(H) + D^\circ(R\text{-}H)$$

Using the data in Table V̄.1 in conjunction with the values obtained above for $D^\circ(R\text{-}H)$ allows calculation of the heats of formation of the ethyl, isopropyl and t-butyl radicals. These calculations are summarised in Table V̄.4.

Table V̄.4:- Heats of Formation of Radicals

Radical R	$\Delta H_f^\circ(RH)$ kcal mole^{-1}	$\Delta H_f^\circ(H)$ kcal mole^{-1}	$D^\circ(R\text{-}H)$ kcal mole^{-1}	$\Delta H_f^\circ(R)$ kcal mole^{-1}
Ethyl	-20.24	52.1	96.4	24.1
i-Propyl	-24.82	52.1	94.2	17.3
t-Butyl	-32.15	52.1	91.1	6.85

V̄.4 Dissociation Energies of C-C Bonds

A knowledge of the heats of formation of radicals allows estimation of the dissociation energy of the carbon to carbon bonds formed when these radicals combine. The relationship used to calculate the bond dissociation values is $D^\circ(\overset{1}{R}\text{-}R) = \Delta H_f^\circ(R) + \Delta H_f^\circ(R^1) - \Delta H_f^\circ(\overset{1}{R}\text{-}R)$

Before/

/Before the value of $D^{o}(R^{1}-R)$ can be calculated the heat of formation of the alkane $R^{1}-R$ must be known. These values can generally be determined from tables [67]. The results of the calculations using the radical heats of formation calculated above are collected in Table V.5.

Table V.5:- Dissociation energies of C-C bonds

Alkane	$\Delta H_f^{o}(R^{1}-R)$ kcal mole^{-1}	R^{1}	R	$D^{o}(R^{1}-R)$ kcal mole^{-1}
n-butane	-30.15	C_2H_5	C_2H_5	78.5
2-methyl butane	-36.92	i-C_3H_7	C_2H_5	78.0
2;2 dimethyl butane	-44.35	t-C_4H_9	C_2H_5	74.8
2;3 dimethyl butane	-42.49	i-C_3H_7	iC_3H_7	76.3
2;2;3 trimethyl butane	-48.96	i-C_3H_7	t-C_4H_9	72.1
2;2;3;3 tetramethyl butane	-53.99	t-C_4H_9	t-C_4H_9	66.5

V.5 Heats of Formation and C-I Bond Strengths of Alkyl Iodides

Early efforts to determine the values of C-I bond strengths led to inaccurate values as the mechanism assumed for the decomposition of the alkyl iodides was incorrect. The re-evaluation of Oggs data[93] for the reaction of HI with methyl iodide by Benson[95] and Sullivan [94], combined with the study of this reaction by Flowers and Benson[96], has led to the value of 54 kcal mole^{-1} being accepted as the C-I bond strength in methyl iodide. Hartley and Benson[97] studied the reaction of HI with ethyl iodide and determined the C-I bond dissociation energy to be 52.0 kcal mole^{-1}. This is in excellent agreement with the result of Carson and his co-workers[111] who determined the C-I bond dissociation energy in ethyl iodide to be 52.2 kcal mole^{-1}, from a study of the reduction of EtI by lithium aluminium hydride/

/hydride in ethereal solution. If the bond dissociation energy of this bond is taken as 52.1 kcal mole^{-1}, the value of ΔH_f° (Et) equal to 24.1 kcal mole^{-1}, as determined above, and the well established value of 24.1 kcal mole^{-1} for ΔH_f° (I)[118] it is possible to determine the value of ΔH_f° (EtI) using the thermochemical relationship,

$$\Delta H_f^\circ (EtI) = \Delta H_f^\circ (Et) + \Delta H_f^\circ (I) - D^\circ (R\text{-}I).$$

The value obtained for ΔH_f° (EtI) is - 2.5 kcal mole^{-1} and this is in agreement with the value of - 2.1 kcal mole^{-1} obtained by Carson[111].

There is no reliable value in the literature for the C-I bond dissociation energy of tertiary butyl iodide, isopropyl iodide or for the heats of formation of these compounds. Using the group additivity value given by Benson[112] for ΔH_f° [C-C(H$_3$)] equal to - 10.08 kcal mole^{-1} and that given by Benson and Amano[60] for [C-C$_2$(H)(I)] as 10.7 kcal mole^{-1} the heat of formation of isopropyl iodide is estimated to be - 9.46 kcal mole^{-1}. The relationship given above then leads to a value of 52.2 kcal mole^{-1} for the C-I bond dissociation energy of isopropyl iodide. A calculation of this type is not possible for tertiary butyl iodide as no group additivity value is available for ΔH_f° [C-(C$_3$)(I)] . However the use of bond additivity values given by Benson[112] results in a value for ΔH_f° (tBuI) of - 12.1 kcal mole^{-1}. This leads to a value for the C-I bond dissociation energy of 44.5 kcal mole^{-1}. This value appears low in comparison with that found for EtI and iPrI and this most probable arises from a high value for ΔH_f° (tBuI) being obtained by the use of bond additivity rules.

Use of the group additivity rules given by Benson[112] results in a value for ΔH_f° (EtI) of - 1.3 kcal mole^{-1}. This results from the following calculation.

$$CH_3 - CH_2I = [C - (C)(H)_3] + [C - (C)(H)_2(I)]$$

$$\Delta H_f^\circ(C_2H_5I) = - 10.08 + 8.8 = -1.3 \text{ kcal mole}^{-1}$$

If/

/If the value of -2.5 kcal mole^{-1}, obtained from the present work, is taken for $\triangle H_f^\circ$ (C_2H_5I) and the partial group contribution for $[C-(C)(H)_3]$ of -10.08 kcal mole^{-1} is assumed to be correct, a new value of 7.9 kcal mole^{-1} is obtained for the group contribution $[C-(C)(H)_2(I)]$.

By considering the thermochemistry of the reaction RI ⟶ A-I + H, (A represents an olefine), it is possible to write the following relationship.

$$D^\circ(RI-H) = \triangle H_f^\circ (AI) + \triangle H_f^\circ(H) - \triangle H_f^\circ (RI)$$

Using the value of $\triangle H_f^\circ(H)$ from Table V.1, the values of $\triangle H_f^\circ(RI)$ calculated above and assuming that the value of $D^\circ(RI-H)$ is equal to $D^\circ(RH-H)$, the values of $\triangle H_f^\circ(AI)$ for A equal to ethylene, propylene and isobutene have been calculated. The value of $D^\circ(R-H)$ was taken equal to 96.4 kcal mole^{-1} as determined above for the C-H bond in ethane. The relationship; $D^\circ(A-I) = \triangle H_f^\circ(A) + \triangle H_f^\circ(I) - \triangle H_f^\circ(A-I)$, was then used to calculate the bond dissociation energy for an iodine atom added to the olefines mentioned above. The values are tabulated along with the other thermochemical information related to iodides in Table V.6.

The negative values obtained for $D^\circ(A-I)$ may be the result of the assumption made above being in error but it would appear reasonable to assume that the A-I bond dissociation energies are close to zero. This agrees with Benson's finding that the rate of isomerisation of cis to trans-butene-2 in the presence of iodine atoms, is dependent on the rate of internal rotation of the iodo-olefine complex and not on the rate of addition, or removal, of the iodine atom to the olefine.

Table V.6/

Table V̄.6

R	$\Delta H_f^{\circ}(R-I)$ kcal.mole^{-1}	$D^{\circ}(R-I)$ kcal.mole^{-1}
Ethyl	-2.5[a]	52.1
iPropyl	-9.46	52.2[b]
tButyl	-12.1	44.5[c]
Ethylene	41.8	-3.8
Propylene	34.8	-3.4
Isobutene	32.0	-2.5

a. Estimated using literature value[97,111] of 52.1 kcal mole^{-1} for D°(Et-I).

b. Estimated with ΔH_f° (PrI) = -9.46 kcal mole^{-1} calculated using group additivity values[112].

c. Estimated with ΔH_f° (tBuI) = -12.6 kcal mole^{-1} using bond additivity values[112].

V̄.6 Polanyi Relationship

Evans and Polanyi[113], by application of simple geometry to the potential energy curves of the species involved in the reactions of alkali metal atoms with alkyl chlorides, deduced that for a series of related metathetical reactions a relationship of the form; $E = \alpha\Delta H + C$ should hold. Here E is the activation energy ΔH is the heat of reaction and α and C are constants. They made no allowance for resonance in the activated complexes. Butler and Polanyi[115] plotted the activation energies of the reaction of sodium atoms with alkyl chloride against C-I bond energies, which they took as representing the graduation of the C-Cl bond energies, and found the data gave a linear plot. The C-I bond strengths were measured on the assumption that the primary step in iodide decomposition was the breaking of the R-I bond. However modern values of the C-Cl bonds do not give a linear relationship

between/

/between the activation energy and the heat of reaction. Fettis and Knox[28] found that the data for the chlorination, bromination and iodination of hydrogen and its isotopes lay on a straight line when the experimental activation energies were plotted against the endothermicities at absolute zero for the reaction $X + H_2 \longrightarrow H + X H$ (X = halogen atom).

Making the assumption that the endothermic chlorine and bromine hydrogen abstractions from hydrocarbons also lay on this line, Fettis and Knox used the experimental activation energies for these reactions to calculate $\triangle H$ values. The R-H bond strengths which could be calculated from these values of $\triangle H$ were in agreement with these values measured by other methods.

The determination of the activation energies of the iodine atom abstraction reactions combined with estimation of the heats of reactions allows additional tests to be made of the Polanyi Relationship. The $\triangle H$ values for the reaction were calculated from the heats of formation of the species H_2, X, RH and XH obtained from tables [67,116] and the heats of formation of the radicals R calculated above. The activation energies for the chlorination and bromination reactions included in the graph were those given by Fettis and Knox[28]. The data is tabulated in Table V.7 and a plot of E(act) against $\triangle H$ is given in figure 27.

The data fall on a line with $\alpha = 0.87$ and $C = 4.5$ kcal mole^{-1}. Inclusion of the data for hydrogen and its isotopes is not entirely justifiable because these reactions do not belong to the same series as the hydrocarbon reactions. The results lie on the same line as the hydrocarbon results. The variation in α for these reactions of Cl, Br and I, i.e. $\alpha(I) > \alpha(Br) > \alpha(Cl)$, predicted by Trotman-Dickenson[114] cannot be detected. It is probable that this variation is so small that it is concealed by experimental error.

The Polanyi relationship allows predictions to be made for the activation energies/

Table V.7:- Data for Polanyi Relationship

	E_{act}	ΔH_f^o				ΔH^o
		X^a	RH^b	XH^a	R^c	
Iodination						
C_2H_6	26.3[c]	+25.5	-20.24	6.2	24.1	25.0
C_3H_8	24.6[c]	+25.2	-24.82	6.2	17.3	22.8
iC_4H_{10}	21.6[c]	+25.5	-32.15	6.2	6.85	19.7
H_2	33.4[d]	+25.5	0	6.2	52.1[a]	32.8
Bromination						
C_2H_6	13.2[d]	+26.7	-20.24	-8.66	24.1	9.0
C_3H_8	9.95[d]	+26.7	-24.82	-8.66	17.3	6.7
$i\text{-}C_4H_{10}$	7.51[d]	+26.7	-32.15	-8.66	6.85	3.64
H_2	19.7[d]	+26.7	0	-8.66	52.1	16.7
Chlorination						
H_2	5.48[d]	+29.0	0	-22.06	52.1	1.04

Units are $kcal.mole^{-1}$

a) Reference 116

b) Reference 67

c) This work

d) Reference 28

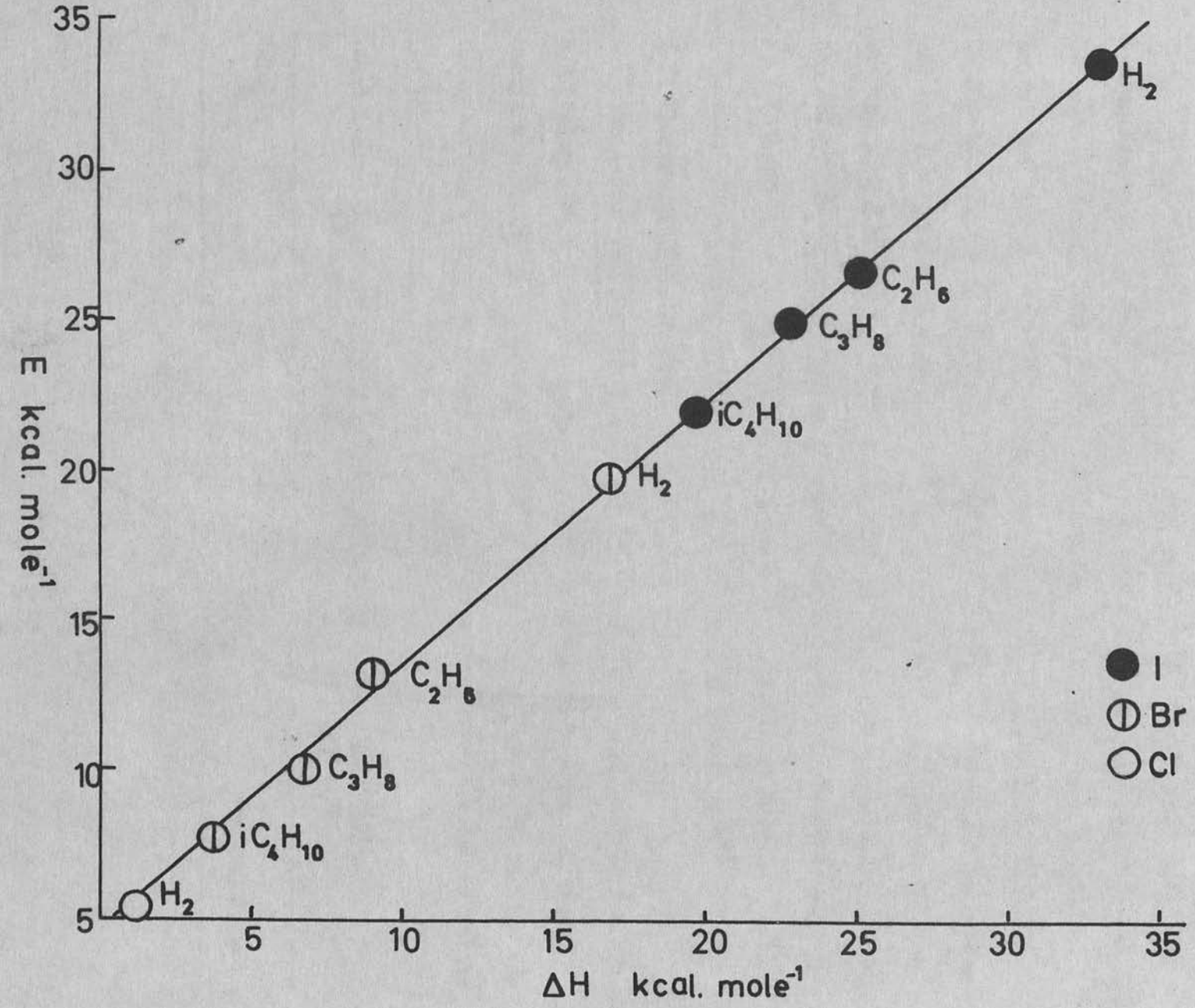


FIGURE-27 POLANYI RELATIONSHIP

/energies of the hydrogen abstraction reactions of iodine from methane and the secondary position in n-butane.

Taking the heats of formation of methyl and the sec-butyl radicals as respectively 33.9 kcal $mole^{-1}$ (reference 116) and 11.0 kcal $mole^{-1}$ (reference 116). The values of $\triangle H(I + RH \longrightarrow HI + R)$ are found to be 31.1 kcal $mole^{-1}$ for methyl and 21.8 kcal $mole^{-1}$ for sec-butyl. The values used in these calculations for $\triangle H_f^{\circ}(CH_4)$ and $\triangle H_f^{\circ}(nC_4H_{10})$ were obtained from reference 67 and had the respective values - 17.9 kcal $mole^{-1}$ and -30.15 kcal $mole^{-1}$. The value of $\triangle H_f^{\circ}(I)$ was taken as 25.5 kcal $mole^{-1}$ (reference 112). Using the Polanyi relationship the activation energies were calculated to be;

Methane $E = 0.87 \times 31.1 + 4.5 = 31.6$ kcal $mole^{-1}$

sec.H in n-Butane $E = 0.87 \times 21.8 + 4.5 = 23.5$ kcal $mole^{-1}$

$\bar{V}$.7 Pre-exponential Factors

The A-factors (per hydrogen atom) for the halogen atom abstraction of a hydrogen atom from ethane, the secondary position in propane and the tertiary position in isobutane are collected in Table $\bar{V}$.8. The results for the reactions other than those of iodine are taken from the review by Fettis and Knox[28].

Table $\bar{V}$.8:- A-factors for hydrogen abstraction from a hydrocarbon by a halogen atom.

Halogen	A-factor x 10^{13} ($mole^{-1}$ c.c. $sec.^{-1}$)			Radical Formed
	C_2H_5	iC_3H_7	tC_4H_9	
F	1.00	0.63	0.70	
Cl	1.5	3.6	2.1	
Br	1.23	2.5	1.95	
I	2.1	9.1	7.6	

The listed A-factors for the bromine atom reactions are lower than those of/

/of the equivalent chlorine atom reactions and this combined with the general trend of increasing A factor in moving from fluorine to iodine leads one to suspect that the tabulated values for bromine atoms are low. The bromination data was obtained by competitive experiment [109] using the absolute value for abstraction of hydrogen from methyl bromide determined by Kistiakowsky and van Artsdalen[118]. It is therefore suggested that the A-factor determined by Kistiakowsky is low by a factor of approximately 2.

V.8 Test of the Transition State Theory

If the assumption is made that the transmission co-efficient is unity and quantum mechanical tunnelling is neglected, the transition state theory gives the A-factor of a metathetical reaction by the following expression.

$$A = e\frac{2kT}{h} \exp\left(\frac{\triangle S_R^* + \triangle S_T^* + \triangle S_V^*}{R}\right)$$

Here the symbols $\triangle S_R^*$, $\triangle S_T^*$ and $\triangle S_V^*$ represent the rotational, translational and vibrational entropies of activation, k is the Boltzman constant, h is Planck's constant and e, R and T have their conventional meaning. It is of interest to compare the theoretical values of A determined by this expression with the experimental value of A as a test of the theory. The value of $\triangle S_T^*$ is obtained by use of the Sackur - Tetrode equation[119]. Taking the standard state as 1 mole cc^{-1} at 298°K the equation takes the form.

$$S_T^\circ = R\left(\frac{5}{2}\ln T + \frac{3}{2}\ln M - \ln P_{atm} - 1.164\right)$$

The value of $\triangle S_T^*$ is then calculated from the following equation:

$$\triangle S_T^* = S_T^\circ(RHI^{\neq}) - S_T^\circ(RH) - S_T^\circ(I)$$

$$= \frac{3}{2} R \ln\left(\frac{M(RHI^{\neq})}{M(RH)}\right) - S_T^\circ(I)$$

The rotational entropy of an assembly of non linear rigid polyatomic molecules/

/molecules is given by:

$$S^{o}_{R} = R\left(\frac{3}{2}\ln T + \frac{1}{2}\ln ABC - \ln\ \right) - 5.384$$

and hence

$$\Delta S^{*}_{R} = \frac{1}{2} R \ln \frac{A^{*}B^{*}C^{*}}{A\ B\ C}$$

The terms $A^{*}B^{*}C^{*}$ and A B C are the products of the moments of inertia of RHI and RH about the principal axes in respectively the complex and molecule. This value of ΔS^{*}_{R} is for a single hydrogen atom of any type and it is necessary to include the symmetry number to obtain the appropriate value for all hydrogens of a given type.

In the present work the values of $A^{*}B^{*}C^{*}$ and A B C have been calculated by a graphical method. The C-C and C-H bond lengths were taken as 1.54 $\overset{o}{A}$ and 1.10$\overset{o}{A}$ respectively and bond angles were assumed to be 109.5^{o} except for the C-H-I bonds in the complex which was assumed linear. The lengths of the half order bonds were determined by applying Paulings rule[120]. This results in an increase of 0.18$\overset{o}{A}$ in the half order bond lengths over the normal bond lengths i.e. C---- H = 1.28$\overset{o}{A}$ and H-----I = 1.78$\overset{o}{A}$. As pointed out by Fettis, Knox and Trotman-Dickenson[121] small changes in molecular dimensions have little effect on the ratio $A^{*}B^{*}C^{*}$/ABC. As the calculations were carried out for the ethane ----- I, iso-propyl -----I and the t-butyl ----I complexes the problem of different configurations of the complex, produced by rotation about C-C bonds, was not present.

To evaluate ΔS^{*}_{V} accurately would require a detailed knowledge of the vibration frequencies of all the bonds in the reactant and complex. Such data is not available and hence evaluation of ΔS^{*}_{V} can only be approximate. The method used here is that of Fettis, Knox and Trotman-Dickenson[121]. The assumption is made that only vibrations intimately associated with the reaction are changed in moving from reactant to the complex. Allowance is

in/

/in fact made for only three of the five vibrational modes which can be included in this category. These are the symmetrical stretching of the C-H-I bond and the doubly degenerate bending mode of this bond. The stretching vibration of the C-H bond which becomes the reaction co-ordinate is included in the term kT/h and the change in frequency of the wagging of the H atom against the hydrocarbon molecule is ignored. This frequency will be reduced greatly by the addition of the mass of the iodine atom and the weakening of the C-H bond. The contribution of this change in frequency to the value of $\Delta S_V^{\ddagger}$ is liable to be as large as that of the bending modes and is neglected basically because of the difficulty in calculating the frequency change rather than because of its lack of importance.

Following Fettis et al.[121], the bending and stretching frequencies have been calculated from values for the frequencies of the bending modes of the H----H----Cl complex calculated by Pitzer[117] from a value for the stretching frequency of this complex derived by Bigeleisen and Wolfsberg[123]. The assumption was made that the force constants of the bonds do not change with R or with the halogen atom. The stretching frequencies were calculated using the formula given below.

$$\nu_{st}(RHI) = \nu_{st}(H_2Cl)\left[\frac{\mu_{H--Cl}}{\mu_{R--I}}\right]^{1/2}$$

The reduced mass μ_{x---y} is given by;

$$\frac{1}{\mu_{x--y}} = \frac{1}{Mx} + \frac{1}{My}$$

where M is the molecular weight of the species denoted by the subscript. The bending frequencies were calculated using the formula

$$\nu_{bend}(RHI) = \nu_{bend}(H_2Cl)\left[\frac{\lambda_{H--Cl}}{\lambda_{R--I}}\right]^{1/2}$$

The values of λ were calculated using a formula derived by Schlapp[119].

$$\frac{1}{\lambda_{x-y}} = \frac{1}{J_x} + \frac{1}{J_y}$$

Here/

/Here $$J_x = I_x + \frac{M_y + M_H}{M_y + M_H + M_x} M_x . a^2$$

and $$J_y = I_y + \frac{M_x + M_H}{M_y + M_H + M_x} M_y . b^2$$

The symbols a and b represent the distances X---H and Y---H measured from the centres of gravity of X and Y to the central H atom. The value of I_R may be calculated from the expression $I_R = (ABC)^{\frac{1}{3}}$.

The entropy values equivalent to the frequencies at 600°K were determined from tables given by Wilson[120].

An unfortunate aspect of the calculations for iodine atoms is that the vibration frequencies tend to be low and hence the values of $\triangle S^*_V$ are large and have a greater influence on the value of $\triangle S^*$ total than is the case with F, Cl and Br. At low frequencies small frequency differences lead to large differences in $\triangle S^*_V$.

The calculations are summarised in Table V.9. Included in this table are values for $\triangle S^*_V$ calculated from the experimental A factor using the theoretical values for $\triangle S^*_R$ and $\triangle S^*_T$.

Table V.9:- Theoretical A-factors

Bond Type	$\triangle S^*_T$	$\triangle S^*_R$	$\triangle S^*_V$(calc)	$\triangle S^*_V$(exp)	logA(calc)	logA(exp)	log $\frac{A_{exp}}{A_{calc}}$
Primary C_2H_6	-17.49	7.60	13.68	10.66	14.79	13.3	-1.49
Secondary C_3H_8	-18.38	5.09	14.70	13.28	14.58	13.96	-0.62
Tertiary iC_4H_{10}	-18.97	4.34	15.54	14.21	14.36	13.88	-0.48

$\triangle S$ units are cal $deg^{-1} mole^{-1}$

A factor values are for a single hydrogen atom of a particular type.

$\triangle S^*_V = S_{stretch} + 2S_{bend}$. The bending mode is doubly degenerate.

The discrepancies between the observed and calculated values for the

'A'/

/'A' factor are larger than those found for these reactions of fluorine[121], chlorine[126] and bromine[127]. This would be expected on the basis of the larger mass of the iodine atom introducing larger values of $\triangle S^{*}_{V}$. A trend may be detected in the deviation of the experimental values from the theoretical values. The theoretical values are all larger than the experimental values and the discrepancy increases from isobutane to ethane. There would appear to be no theoretical explanation for the theoretical values being greater than the experimental values. The vibrational modes which were not considered in the calculation of $\triangle S^{*}_{V}$ would be expected to contribute positive values to the entropy of vibration of the complex and hence to $\triangle S^{*}$.

V.9 Influence of Inhibition Reactions

Application of the steady state treatment to the iodination mechanism yields the rate law (page 35),

$$\frac{d\left((RI) + (A)\right)}{dt} = \frac{(I)\left(k_2k_3(I_2)(RH) - k_7k_4k_5(A)(HI)^2/k_8\right)}{k_3(I_2) + k_4(HI)}$$

Replacing (I) by $K_{I_2}(I_2)^{\frac{1}{2}}$, where K_{I_2} equals the iodine molecule dissociation equilibrium constant, and re-arranging gives the rate law in the following form

$$\frac{d\left((RI) + (A)\right)}{dt} = \frac{K_{I_2}\, k_2(I_2)^{\frac{1}{2}}\left((I_2)(RH) - K^{-1}(A)(HI)^2\right)}{k_4(HI)/k_3 + (I_2)}$$

In this expression $K = k_2k_3k_8/k_4k_5k_7$, i.e. the equilibrium constant for the overall reaction;

$$I_2 + RH \rightleftharpoons A + 2HI \ .$$

Of the terms in the right hand side of the above rate equation the equilibrium constants K_{I_2} and K can be calculated from thermodynamic data and the rate constant k_2 has been determined from the measurements of the reaction rate in the initial reaction stages, i.e. $(HI) \sim 0$. The concentrations of the different/

/different species can be calculated at any time, by use of reaction stoichiometry, provided the quantity of product is known. The rate constant ratio k_4/k_3 is unknown. If a series of reactions are carried out with mixtures of initially constant composition and pressure, but of different duration, a product/time curve can be constructed and by drawing tangents to this curve the rate of reaction, at any point in time $d\left((RI) + (A)\right)/dt$, can be estimated approximately. The product/time curve also yields the concentration of products, (RI) + (A), at any time. By combining measurements of the reaction rate with calculation of the value of the right hand side of the above rate equation, for a range of possible values of the ratio k_4/k_3, it is possible to obtain an estimate of the magnitude of k_4/k_3. This method of estimating k_4/k_3 is fairer than calculating the value of k_4/k_3 directly from the reaction rate estimate and the other known values, using the rate expression given above, as it allows information to be gained regarding the change in value of the right hand side of the rate expression with variation in the value of k_4/k_3. This is of particular importance when one considers the inaccuracies involved in tangent drawing and the lack of sensitivity of the right hand side of the rate equation to variations in the ratio k_4/k_3 when the HI concentration is low. This technique has been applied to a small number of runs for the I_2/isobutane, I_2/propane and I_2/ethane systems.

The ratio k_4/k_3 has been determined by Benson and his co-workers for the t-butyl and iso-propyl radicals. The value of k_4/k_3 found for the t-butyl radical was 0.25 and that for the iso-propyl radical was 2. Williams and Ogg[128] studied the attack of H atoms, produced by photolysis of HI in the presence of I_2, on HI and I_2 and found that $k_{H_2}/k_{I_2} = 0.28$. Fettis and Trotman-Dickenson[109] studied the attack of ethyl radicals, produced by the photolysis of methyl ethyl ketone, on I_2 and HBr. by a competitive method. They worked in the temperature range 50-110°C and found the ratio k_{EtH}/k_{EtI} /

/k_{EtH}/k_{EtI} to vary between 0.025, at the lower temperature, and 0.04. Benson's result for the t-butyl radical of 0.25 for k_4/k_3 agrees with the results discussed above. Predictions of the value of k_4/k_3, from a consideration of the strengths of the bond under attack, would lead to a value less than one. The heats of reaction of R with HI are respectively -25.04, -22.8 and -20.0 kcal $mole^{-1}$ for ethyl, isopropyl and t-butyl while the attack of these radicals on I_2 are respectively -16, -16.2 and -8.3 kcal $mole^{-1}$ exothermic if the ΔH_f° (RI) values calculated previously are correct. On the basis of reaction heat the attack on HI would appear to be favoured. It is therefore of interest to obtain estimates for k_4/k_3 for isobutane and propane and compare these with Benson's results.

Small variations in the initial pressures and compositions of the reaction mixture were a source of error in the experimental determination of the product/time curve. However these variations were at the most 3% and the fact that calculations were carried out on the smooth curves drawn through the experimental points would result in these errors having less influence on the product/time curves. The drawing of tangents to these product - time curves involved personal judgment and hence was a possible source of large errors. The error in tangent drawing has been estimated at ± 15% and this enables a decision to be made between extreme values of the ratio k_4/k_3, e.g. 0.25 and 2 for this ratio for the propyl radical, except in cases where the (HI) concentration is very small and hence the rate expression is insensitive to changes in the value of k_4/k_3.

For the isobutane system two product/time curves have been considered. The data from Tables IV.46 (initial iodine concentration = 9.69×10^{-8} moles cc^{-1}) and IV.42 was plotted and the reaction rate estimated at a number of reaction times. To obtain values for reactant and product concentrations the following/

/following relationships, derived from reaction stoichiometry were used.

$(HI)_t = 2(iC_4H_8)_t$, $(I_2)_t = (I_2)^\circ - \frac{1}{2}(HI)_t$, $(iC_4H_{10})_t = (iC_4H_{10}) - (iC_4H_8)_t$

Subscript t indicates concentrations at time t. $(I_2)^\circ$ and $(iC_4H_{10})^\circ$ are the initial concentrations of reactants. The value of $(iC_4H_8)_t$ was obtained from the product/time plot. The right hand side of the rate equation was estimated, at each of the reaction times, for k_4/k_3 equal to 1, 0.5, 0.25 and 0.1. The data related to these calculations is given in Table V.10 and the product/time curves in figures 28 and 29. The data for reaction--1 at 2000 seconds and reaction - 2 at 6000 seconds agrees with a value of 0.25 for the ratio k_4/k_3. As reaction - 1 proceeds the ratio k_4/k_3 increases in value while the opposite is the case for reaction -2. The variation in k_4/k_3 and the disagreement between reactions-1 and-2 may be produced by experimental error. An unfortunate aspect of the calculations is that the product/time curve tends to flatten, and hence accurate tangent drawing becomes more difficult, in the region where (HI) is large and the rate expression is sensitive to variation in k_4/k_3.

The ratio k_4/k_3 for the i-propyl radical was estimated using the method described above. The following relationships were used to calculate product and reactant concentrations at time(t).

$(HI)_t = 2(C_3H_6)_t + (RI)_t$, $(I_2)_t = (I_2)^\circ - \frac{1}{2}(HI)_t - \frac{1}{2}(PrI)_t$

$(C_3H_8)_t = (C_3H_8)^\circ - (C_3H_6)_t - (PrI)_t$

At any reaction time the value of $(C_3H_6)_t + (PrI)_t$ could be estimated from the product/time curve. To obtain the values of $(C_3H_6)_t$ and $(PrI)_t$ separately the graph of % iodide in the products against reaction time was plotted and from this curve it was possible to estimate the ratio of iodide to olefine in the products at any time. The product time curves and the % iodide plots are given in figures 30, 31 and 32. The results of the calculations/

Table V.10

Reaction Time (secs.)	$(HI) \times 10^8$ moles cc^{-1}	Experimental Rate $\times 10^{12}$ moles $cc^{-1} sec^{-1}$	Theoretical Rate $\times 10^{12}$ moles $cc^{-1} sec^{-1}$			
			$\frac{k_4}{k_3} = 1$	$\frac{k_4}{k_3} = 0.5$	$\frac{k_4}{k_3} = 0.25$	$\frac{k_4}{k_3} = 0.1$
Reaction - 1						
2000	7.20	11.0	7.22	9.8	11.8	13.6
5000	11.32	3.91	2.41	3.81	5.31	7.15
10000	13.20	1.33	1.08	1.80	2.75	3.99
Reaction - 2						
6000	14.4	5.25	2.29	3.58	5.00	6.60
10,000	17.64	2.44	0.51	0.87	1.34	2.0
12,000	18.20	2.16	0.49	0.83	1.10	1.95

Reaction - 1 $(I_2)^\circ = 9.69 \times 10^{-8}$ moles cc^{-1}, $(iC_4H_{10})^\circ = 2.63 \times 10^{-7}$

Temperature = 306.4°C $K = 5.16 \times 10^{-7}$ moles cc^{-1}

Reaction - 2 $(I_2)^\circ = 1.27 \times 10^{-7}$ moles cc^{-1}, $(iC_4H_{10})^\circ = 4.17 \times 10^{-7}$ moles cc^{-1}

Temperature = 296.7°C $K = 3.36 \times 10^{-7}$ moles cc^{-1}

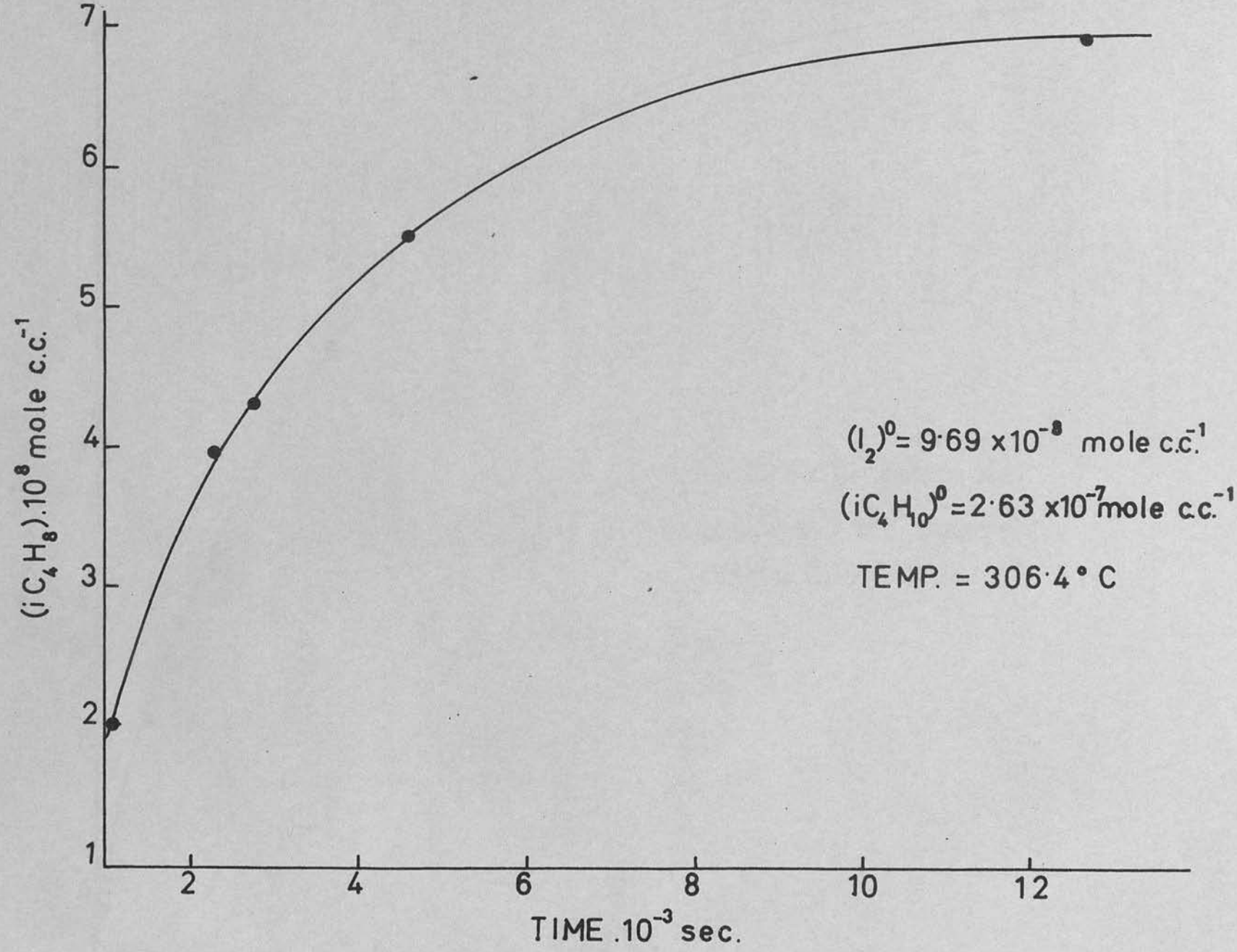


FIGURE-28 IODINE + ISOBUTANE PRODUCT/TIME PLOT

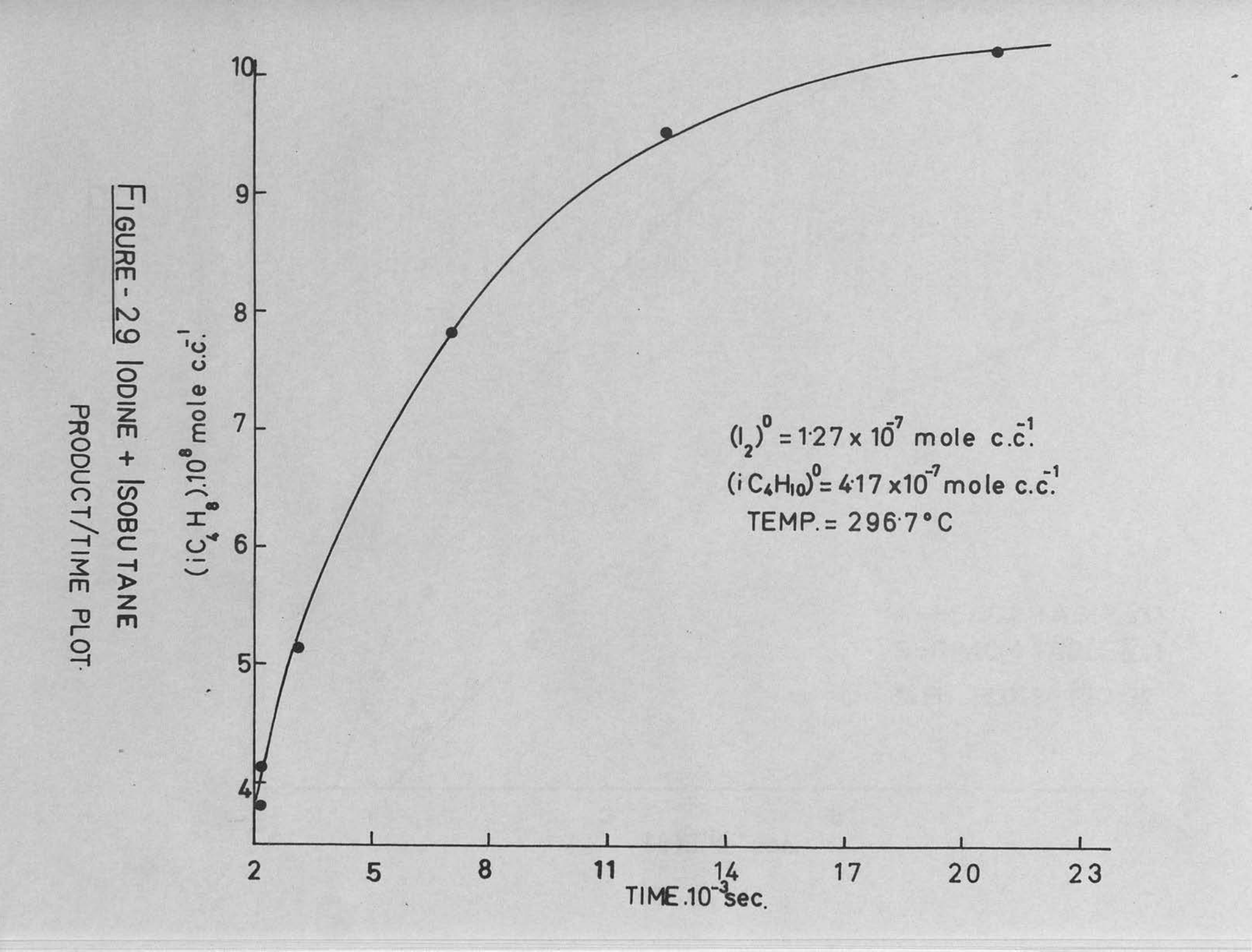


FIGURE - 29 IODINE + ISOBUTANE

PRODUCT/TIME PLOT.

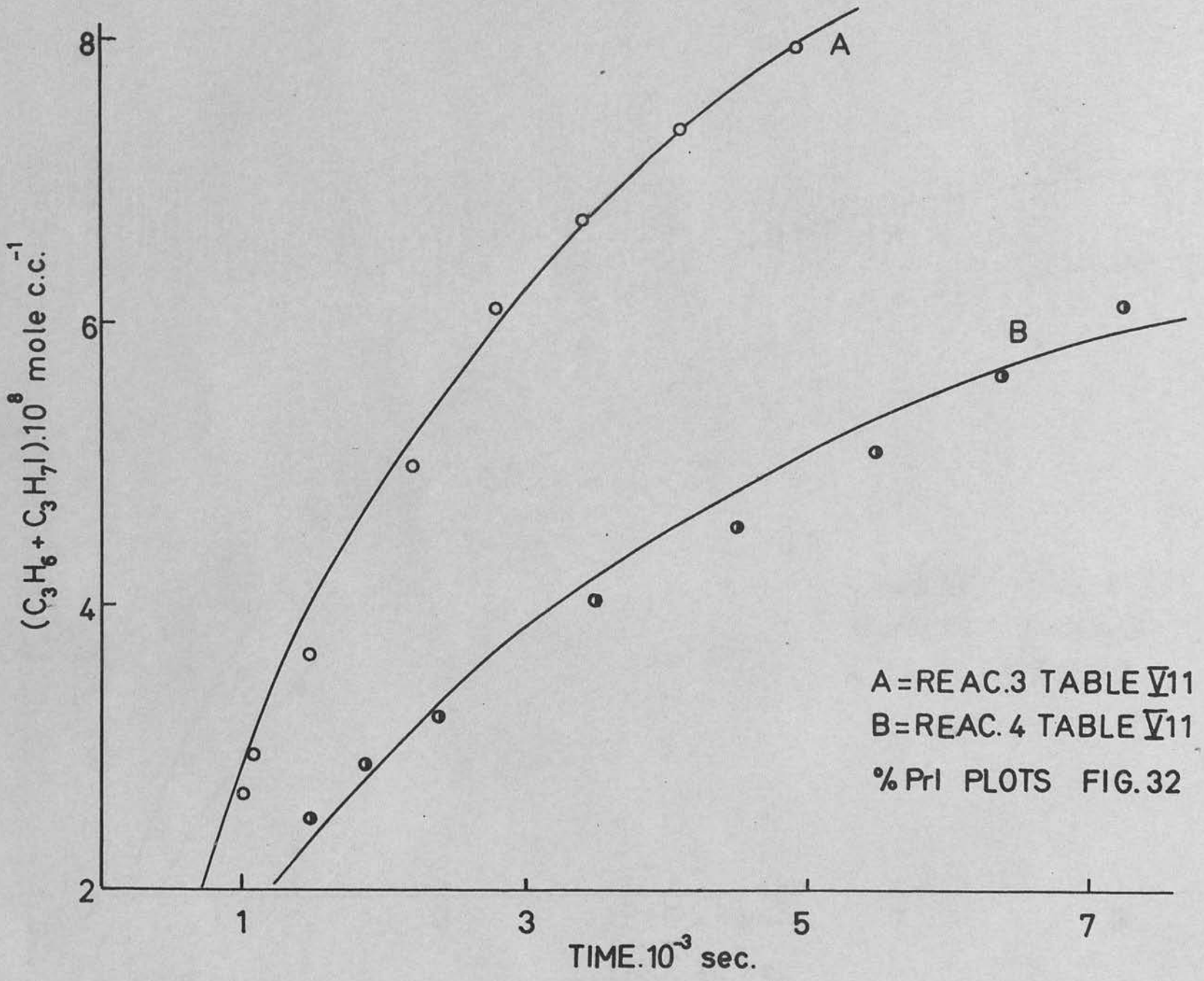


FIGURE-30 IODINE + PROPANE PRODUCT/TIME PLOTS

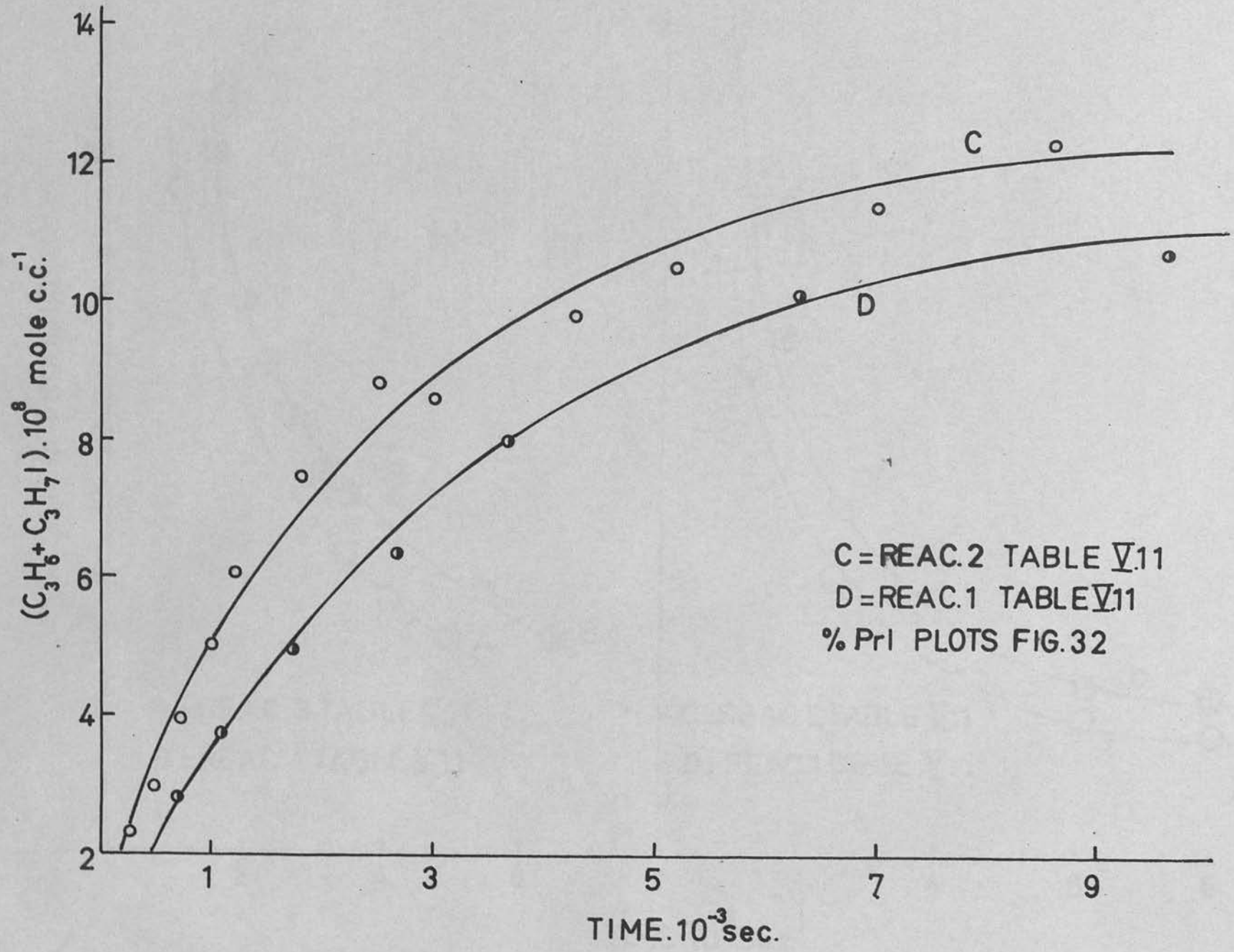


FIGURE-31 IODINE + PROPANE PRODUCT/TIME PLOT

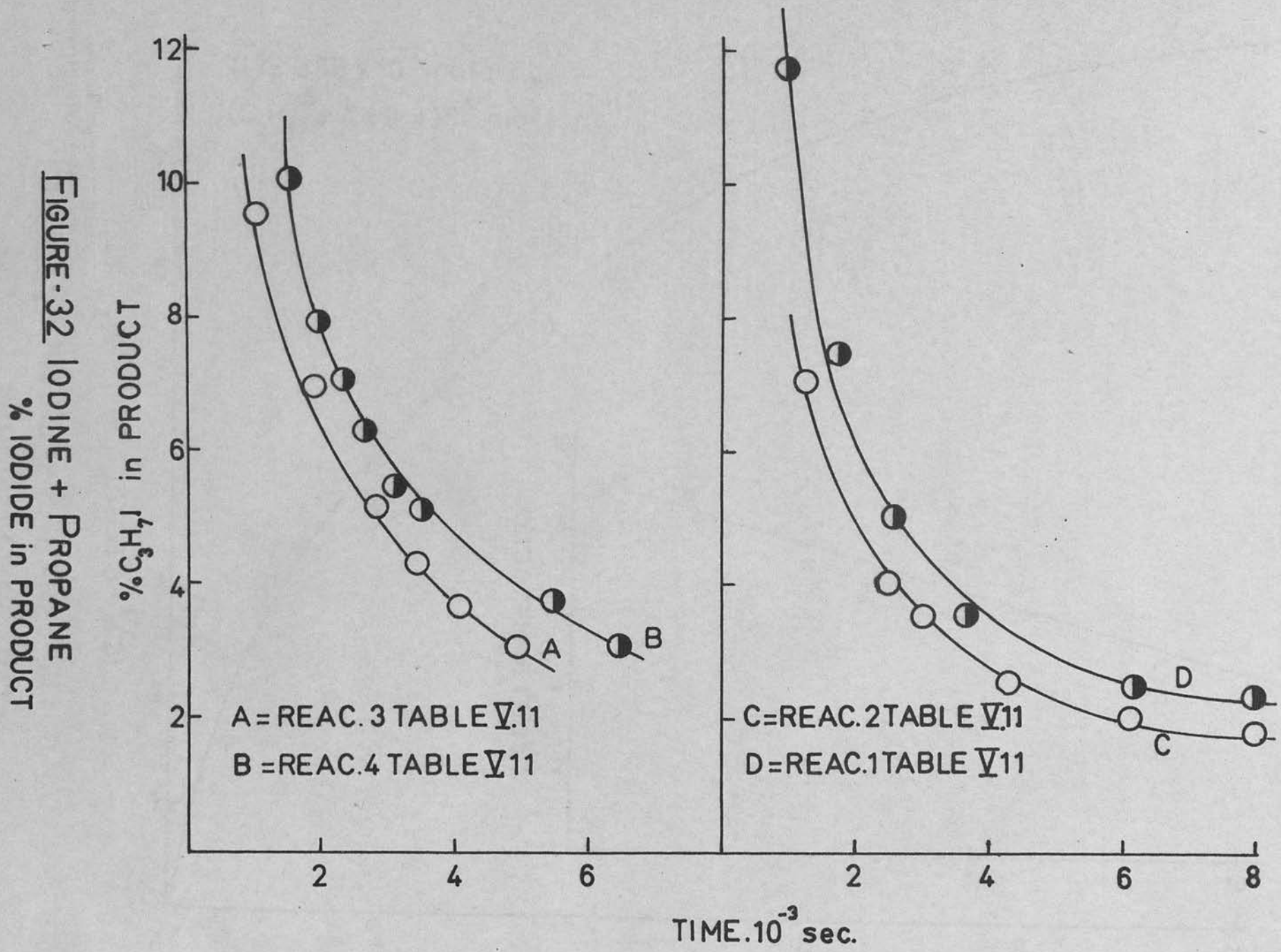


FIGURE-32 IODINE + PROPANE
% IODIDE in PRODUCT

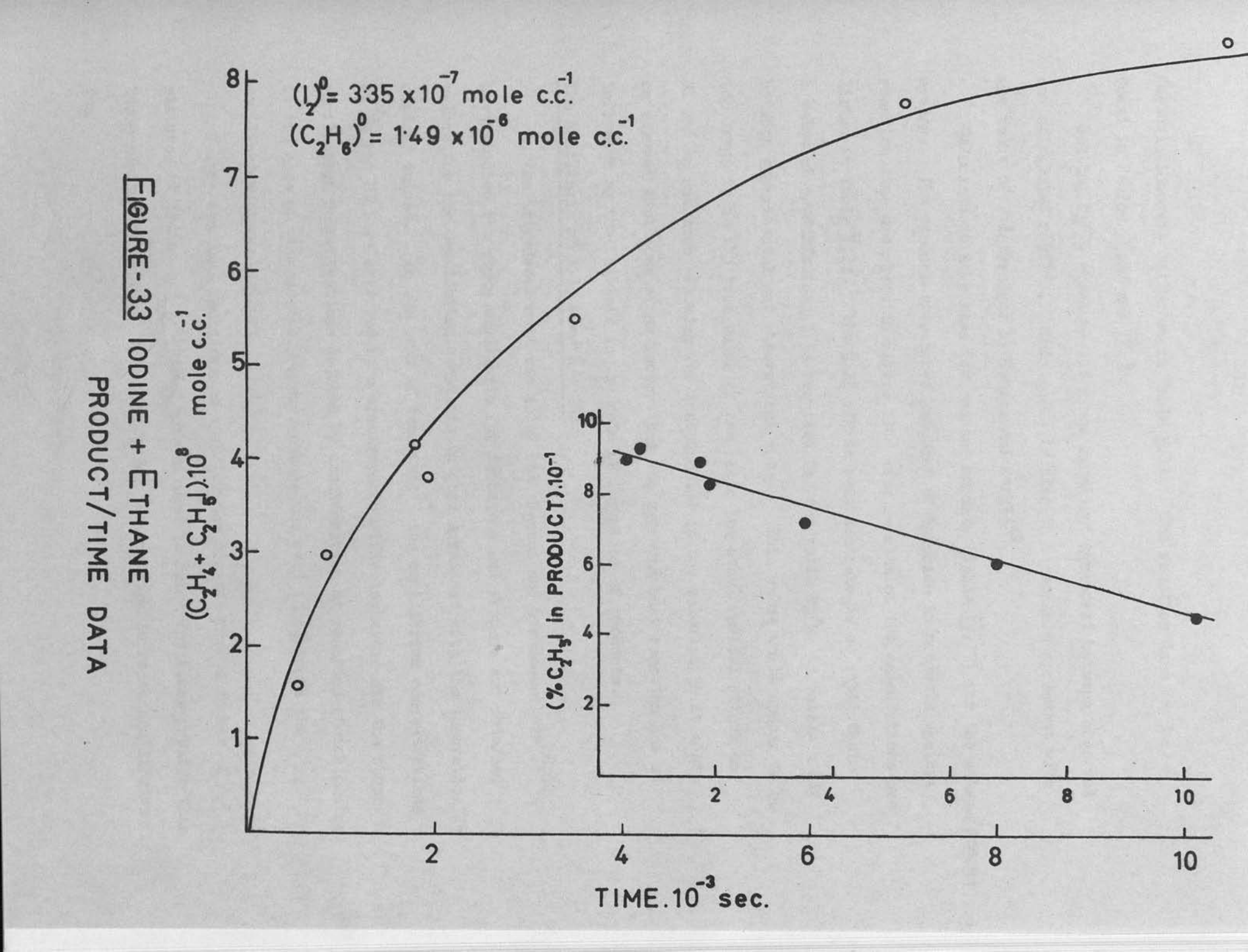


FIGURE-33 IODINE + ETHANE PRODUCT/TIME DATA

/calculations are collected in Table V.11. The reaction data may be found in Tables IV.27 and IV.29.

Setting k_4/k_3 equal to 1.5 gives excellent agreement between observed and calculated results. This value is also in reasonable agreement with the value of 2 determined by Benson and Nangia[47].

Calculations were made for one set of data (Table IV.17) for the ethane/iodine system. The product-time curve and plot of % iodide in products against reaction time are given in figure 33. The results of the calculations are listed in Table V.12. The fall off in reaction rate is so rapid that a value of approximately 7 is required for the ratio k_4/k_3 to obtain a fit between experimental and theoretical rates. This value would appear to be too large to be the true value of the ratio for ethyl radical attack on HI and I_2 and even allowing for inaccuracies in the calculation it must be assumed that some other factor than the expected back reaction has an influence on the fall off in the rate of formation of products.

The Equilibria $RH + I_2 \rightleftharpoons A + 2HI$

In the introduction it was noted that Benson and his co-workers[48,51] have studied the above equilibria for isobutane and propane and obtained values for the equilibrium constants in good agreement with the theoretically derived values. In the case of isobutane[51] the equilibrium concentrations of I_2 and HI were measured by a spectrophotometric technique and the other equilibrium concentrations deduced by consideration of reaction stoichiometry. In the case of propane the pressure change was used to estimate the equilibrium concentrations.

Using the same technique as that for the kinetic runs a number of mixtures of iodine and isobutane were allowed to react for times greater than those claimed by Benson[50] as adequate for the reaction to reach equilibrium.

The/

Table V.11:- The ratio $\frac{k_4}{k_3}$ for the i-propyl radical.

Reaction Time secs.	$(HI) \times 10^8$ moles cc^{-1}	Experimental Rate x 10^{12} moles $cc^{-1} sec^{-1}$	Theoretical Rate x 10^{12} moles $cc^{-1} sec^{-1}$ $\frac{k_4}{k_3} = 2$	$\frac{k_4}{k_3} = 1.5$	$\frac{k_4}{k_3} = 1.0$	$\frac{k_4}{k_3} = 0.5$
Reaction - 1						
2000	10.94	17.3	15.0	17.7	21.4	27.2
3000	14.20	14.1	11.0	13.6	16.7	22.3
4000	16.53	10.3	7.7	9.4	12.1	17.0
Reaction - 2						
2000	14.71	20.2	15.9	19.5	25.1	35.5
3000	17.92	12.5	10.1	12.5	16.8	25.2
4000	20.0	8.0	6.99	8.8	12.0	18.7
Reaction - 3						
2000	9.41	17.4	14.7	17.3	20.8	26.4
3000	12.99	11.6	9.55	11.15	14.7	20.0
4000	14.97	9.5	7.3	9.0	11.6	16.5
Reaction - 4						
2000	5.4	11.2	9.9	11.0	12.3	14.0
3000	7.31	8.85	7.96	9.03	10.45	12.24
4000	8.71	7.20	6.74	778	9.19	11.2

Reaction - 1 $(I_2)^\circ = 2.05 \times 10^{-7}$ moles cc^{-1} $(C_3H_8)^\circ = 7.70 \times 10^{-7}$ moles cc^{-1}
Temperature = 328.7°C $K = 1.91 \times 10^{-7}$ moles cc^{-1}

Reaction - 2 $(I_2)^\circ = 1.81 \times 10^{-7}$ moles cc^{-1} $(C_3H_8)^\circ = 1.44 \times 10^{-6}$ moles cc^{-1}
Temperature = 328.7°C $K = 1.91 \times 10^{-7}$ moles cc^{-1}

Reaction - 3 $(I_2)^\circ$ 17.9×10^{-8} moles cc^{-1} $(C_3H_8)^\circ = 13.1 \times 10^{-7}$ moles cc^{-1}
Temperature = 319.3°C $K = 1.28 \times 10^{-7}$ moles cc^{-1}

Reaction - 4 $(I_2)^\circ = 19.8 \times 10^{-8}$ moles cc^{-1} $(C_3H_8)^\circ = 5.18 \times 10^{-7}$ moles cc^{-1}
Temperature = 319.3°C $K = 1.28 \times 10^{-7}$ moles cc^{-1}

Table V.12:- The ratio k_4/k_3 for the ethyl radical

Reaction Time secs.	(HI)x10^8 moles cc^{-1}	Experimental Rate x10^{12} moles $cc^{-1}sec^{-1}$	Theoretical Rate x10^{12} moles $cc^{-1}sec^{-1}$ $\frac{k_4}{k_3}=5$	$\frac{k_4}{k_3}=6$	$\frac{k_4}{k_3}=7$	$\frac{k_4}{k_3}=8$
2000	5.10	14.9	15.8	14.9	13.3	12.4
3000	6.89	10.6	12.8	11.5	10.5	9.6
4000	8.32	7.31	11.0	10.0	8.8	8.05

Table V.14:- Secondary Products

Reactant Hydrocarbon	Pressure of Hydrocarbon	Pressure of Iodine	Temperature of Reaction Vessel	Duration of Reaction	Column* used for analysis	Secondary Product detected	$\frac{SP_x100}{RH}$ + 1
n-butane	4 cms.	1 cm.	260°C	7 hours	No. 4	o-xylene	1.0
i-butane	4 cms.	1 cm.	260°C	7 hours	No. 4	p-xylene	1.0
propane	4 cms.	1 cm.	315°C	5 hours	No. 2	benzene	0.5
ethane	4 cms.	1 cm.	320°C	6 hours	No. 4	butadiene	0.1

* The numbers refer to Table III.1

+ SP = secondary product.

Table V.13

Equilibrium Studies

Reaction Time hours	T°C	Initial Pressures $P(I_2)$ cms.	Initial Pressures $P(iC_4H_{10})$ cms.	Equilibrium Pressures $P(I_2)$ cms.	Equilibrium Pressures $P(iC_4H_{10})$ cms.	Equilibrium Pressures $P(iC_4H_8)$ cms.	$K_p = \frac{4(iC_4H_8)^3}{(I_2)(iC_4H_{10})}$ atms. x 10^3
16	306.5	2.01	2.97	1.4	2.36	0.61	20.1
16	306.5	0.35	0.975	0.015	0.645	0.335	20.5
16	295.7	0.73	1.87	0.286	1.426	0.444	11.2
24	286.5	0.87	2.78	0.47	2.38	0.399	3.2
14	286.5	0.87	2.70	0.485	2.315	0.38	2.66
15	286.5	0.87	0.27	0.52	2.35	0.35	1.85
16	277.3	0.84	2.39	0.495	2.045	0.345	2.25
14	277.3	0.84	2.36	0.462	1.98	0.38	3.1
15	277.3	0.84	2.39	0.535	2.085	0.305	1.3
30	247.6	1.02	3.43	0.80	3.21	0.22	0.22
17	247.8	1.02	3.53	0.775	3.285	0.245	0.30
17	248.0	1.43	3.40	1.15	3.12	0.28	0.54
24	248.0	1.02	3.55	0.70	3.23	0.32	0.73
14	248.0	0.67	5.64	0.24	5.21	0.43	0.88
90	236.2	1.15	5.95	0.93	5.73	0.22	0.105
67	226.2	1.45	5.33	1.29	5.17	0.16	0.032
67	226.2	0.88	6.17	0.69	5.98	0.19	0.087

FIGURE-34 IODINE + ISOBUTANE

ARRHENIUS PLOT FOR THE

OVERALL EQUILIBRIUM CONSTANT

/The isobutene and isobutane were then measured by chromatography and the equilibrium concentrations of HI and I_2 were estimated. The value of K_p was calculated from the following expression.

$$K_p = \frac{(iC_4H_8)(HI)^2}{(iC_4H_{10})(I_2)}$$

The experimental detail and values obtained for K_p are given in Table V.13. An Arrhenius plot for K_p is given in figure 34.

The spread of the values obtained for K_p is large but this can be explained on the basis of experimental error. An error of 5% in iC_4H_8 results in an error of 25% in K_p. At the higher temperature (~300°C) the values of K_p obtained in the present work agree reasonably well with the theoretical value but as the temperature decreases the values fall away from the theoretical and at 250°C they are low by a factor of ten.

There appears to be no obvious method by which these results can be reconciled with those of Benson.

Detection of Secondary Products

Raley and his co-workers[53] in studying the high temperature (~600°C) reactions of iodine with hydrocarbons found that secondary products could be detected. These products were o-xylene with n-butane, p-xylene with isobutane, butadiene with ethane and benzene with propane. Consideration of the discrepancies between the expected and the experimental results for the fall off region suggested that the formation of secondary products could possibly occur at the temperatures at which the studies discussed above were carried out. The results of reactions carried out to test for the presence of secondary products are tabulated along with the experimental detail in Table V.14. The yield of secondary products detected could not be measured accurately in every case owing to the broad shape of the chromatography/

/chromatography peak. The only method used to check the identity of a secondary product was its retention time and analysis was only made for those compounds detected by Raley[53] and mentioned above.

The tabulated results indicate that secondary products are formed in the reactions of iodine with hydrocarbons in the region of 300°C. In order to determine the importance of these reactions an apparatus which would allow a complete and accurate analysis of the secondary products over a range of conditions will be required. It is of some interest to suggest a possible mechanism for the formation of these products and here the production of benzene from propane is taken as an example. A mechanism which would appear possible is given below.

$$CH_3-CH_2-CH_3 \xrightarrow{I_2} CH_3CH=CH_2 \xrightarrow{I} CH_2\cdots CH\cdots CH_2 \quad A$$

$$2\,CH_2\cdots CH\cdots CH_2 \longrightarrow \underset{\text{di-allyl}}{CH_2=CH-CH_2-CH_2-CH=CH_2}$$

$$CH_2\cdots CH\cdots CH_2 + CH_3-CH=CH_2 \longrightarrow CH_2=CH-CH_2-CH_2-\dot{C}H-CH_3$$

$$CH_2=CH-CH_2-CH_2-\dot{C}H-CH_3 \xrightarrow{I} \underset{\text{di-allyl}}{CH_2=CH-CH_2-CH_2-CH=CH_2}$$

Straight chain compounds such as diallyl have been shown by Raley and his co-workers[54] to be converted to aromatics in the presence of iodine. The important step in the above mechanism is the abstraction of an allylic hydrogen from propylene to form the allylic radical A. This type of abstraction has been found to occur readily with butene - 1, resulting in the formation of butadiene, in this work and has also been reported by Benson, Egger and Golden[64] and by Raley, Mullineaux and Bittner[53]. The formation of di-iodides by the addition of I_2 to an olefine could occur in these/

/these systems at low temperatures but in the region of 300°C these compounds are extremely unstable as can be verified by calculation using the thermodynamic data given in the introduction (page 22).

The above results indicate that the atomic chain mechanism, operating in the initial stages of the reaction of iodine with hydrocarbons, is complicated in the later stages by iodine atom attack on the olefines formed by the decomposition of the iodides initially produced by the chain mechanism. The allylic radicals formed lead in turn to hydrocarbon products of higher carbon number than the initial reactant. To confirm the details of the mechanism for these reactions will require apparatus with which one is able to analyse in detail for the secondary products. To obtain a complete picture it should also include a spectrophotometer which will allow the change in I_2 and HI concentration to be followed. An excellent starting point for an investigation would be the reaction of iodine with propylene as the dimerisation reaction would then be expected to be of greater importance in the initial stages, than the formation of propane which would be formed by the addition of HI to the propylene.

REFERENCES

1. M. Bodenstein, Z. phys. Chem., 13 (1894) 56, 22 (1897) 1.
2. M. Bodenstein and S.C. Lind, Z. phys. Chem., 57 (1906) 168.
3. J.A. Christiansen, Kgl. danske Videnskab. Selskab, Mat.-fys. Medd.,1 (1919) 14.
4. K.F. Hertzfeld, Ann. Physik,57 (1919) 635.
5. M. Polanyi, Z. Elektrochem, 26 (1920) 49.
6. W. Nernst, Z. Elektrochem, 24 (1918) 335.
7. W. Nernst, Z. Physik, 21 (1920) 602.
8. S. Arrhenius, Z. phys. Chem., 4 (1889) 226.
9. F. London, Z. Elektrochem, 35 (1929) 57.
10. S. Glasstone, H. Eyring, K. Laidler, The Theory of Rate Processes, McGraw Hill, 1964, page 77.
11. Reference 10, page 88.
12. Reference 10, page 100.
13. H. Eyring and M. Polanyi, Z. phys. Chem., B. 12 (1931) 279
14. K.H. Geib and P. Harteck, Z. phys. Chem., Bodenstein Festband (1931) 849.
15. A. Farkas, Z. phys. Chem.,B10 (1930)419
16. W.C. McLewis, J. Chem. Soc., 113 (1918) 471
17. Reference 10, page 10.
18. K.J. Laidler, Reaction Kinetics, Vol. 1,Pergamon Press. 1963, page 81.
19. C.N. Hinshelwood, Proc. Roy. Soc., A, 113 (1926) 230.
20. R.P. Bell, Trans. Faraday Soc., 37 (1944) 493.
21. F. Paneth and W. Holditz, Ber. (Chem. Ber.), 62 (1929) 1335.
22. F. Paneth and W. Lautsch, Ber. (Chem. Ber.), 64 (1931) 2702.
23. H.S. Taylor and W.H. Jones, J. Amer. Chem. Soc., 52 (1930) 1111.
24. S.W. Benson and J.H. Buss, J. Chem. Phys., 28 (1958) 301.
25. G.C. Fettis, J.H. Knox and A.F.Trotman-Dickenson, J. Chem. Soc., 218 (1960) 1064.

26.	J.H. Knox,	Chem. and Ind., 33 (1955) 1931.
27.	J.H. Knox and R.L. Nelson,	Trans. Faraday Soc., 55 (1959) 937.
28.	G.C. Fettis and J.H. Knox,	Progress in Reaction Kinetics, Vol. 2, Pergamon, 1964
29.	M. Bodenstein,	Z. phys. Chem., 29 (1898) 295.
30.	G.B. Kistiakowsky,	J. Amer. Chem. Soc., 50 (1928) 2315.
31.	B. Lewis and E.K. Rideal,	J. Amer. Chem. Soc., 48 (1926) 2553.
32.	A.H. Taylor and R.H. Crist,	J. Amer. Chem. Soc., 65 (1941) 1377
33.	W.M. Graven,	J. Amer. Chem. Soc., 78 (1956) 3297.
34.	E.M. Magee,	J. Amer. Chem. Soc., 79 (1957) 5375
35.	K. Geib and A. Lendle,	Z. phys. Chem.,B32 (1936) 178.
36.	J.C.L. Blagg and G.A. Murphay,	J. Chem. Phys.,4 (1936) 631.
37.	N.F.H. Bright and R.P. Hagerty,	Trans. Faraday Soc., 43 (1947)647.
38.	L.S. Kassel,	The Kinetics of Homogeneous Gas Reactions, Chemical Catalog Co. Inc., 1932, page 148.
39.	S.W. Benson and R. Srinivasan,	J. Chem. Phys., 23 (1955) 200.
40.	M. Bodenstein and W. Jost,	J. Amer. Chem. Soc., 49 (1927) 1416.
41.	E.J. Rosenbaum and T.R. Hogness,	J. Chem. Phys., 2 (1934) 267.
42.	P.H. Emmet (editor)	Catalysis (Reinhold), vol. III, page3.
43.	J.H. Sullivan,	J. Chem. Phys., 30 (1959) 1292.
44.	J.H. Sullivan,	J. Chem. Phys., 30 (1959) 1577.
45.	J.H. Sullivan,	J. Chem. Phys., 36 (1962) 1925.
46.	O. Horie, Y. Ishi and A. Amano,	J. Phys. Chem., 68 (1964) 1264.
47.	S.W. Benson and P.S. Nangia,	J. Amer. Chem. Soc.,86 (1964) 2773.
48.	S.W. Benson and P.S. Nangia,	J. Amer. Chem. Soc.,86 (1964) 2770.
49.	S.W. Benson and A. Bose,	J. Chem. Phys., 37 (1962) 1081.
50.	S.W. Benson and H. Teranishi,	J. Amer. Chem. Soc., 85 (1963) 2887.
51.	S.W. Benson and H. Teranishi,	J. Amer. Chem. Soc., 85 (1963) 2890.
52.	S.W. Benson and A. Bose,	J. Chem. Phys., 38 (1963) 878.
53.	J.H. Raley,/	

53. /J.H. Raley, R.D. Mullineaux and C.W. Bittner, J. Amer. Chem. Soc., 85 (1963) 3174.

54. J.H. Raley, R.D. Mullineaux and C.W. Bittner, J. Amer. Chem. Soc., 85 (1963) 3178.

55. J.H. Raley, R.D. Mullineaux and C.W. Bittner, J. Amer. Chem. Soc., 85 (1963) 3180.

56. R. Ogg and W. Priest, J. Chem. Phys., 7 (1939) 736.

57. S.W. Benson, J. Chem. Phys., 34 (1961) 521.

58. G.R. Cuthbertson and G.B. Kistiakowsky, J. Chem. Phys., 3 (1935) 631.

59. A. Abrams and T.W. Davies, J. Amer. Chem. Soc., 76 (1954) 5993.

60. S.W. Benson and A. Amano, J. Chem. Phys., 36 (1962) 3464.

61. S.W. Benson and A.N. Bose, J. Amer. Chem. Soc., 85 (1963) 1385.

62. S.W. Benson, A. Bose and P.S. Nangia, J. Amer. Chem. Soc., 85 (1963) 1388.

63. S.W. Benson, D.M. Golden and K.W. Egger, J. Amer. Chem. Soc., 86 (1964) 5416.

64. S.W. Benson, D.M. Golden and K.W. Egger, J. Amer. Chem. Soc., 86 (1964) 5420.

65. S.W. Benson, D.M. Golden and K.W. Egger, J. Amer. Chem. Soc., 87 (1965) 468.

66. H.H. Voge and N.C. May, J. Amer. Chem. Soc., 68 (1946) 550.

67. Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, American Petroleum Institute, Carnegie Press, 1953.

68. M.H. Back and R.J. Cvetanovic, Canad. J. Chem., 41 (1963) 1396.

69. M.H. Back and R.J. Cvetanovic, Canad. J. Chem., 41 (1963) 1406.

70. E. Rabinowitch and W.C. Wood, J. Chem. Phys., 4 (1936) 497.

71. G.K. Rollefson and H. Eyring, J. Amer. Chem. Soc., 54 (1932) 170.

72. M.I. Christie, A.J. Harrison, R.G.W. Norrish and G. Porter, Proc. Roy. Soc., A231 (1955) 446.

73. K.E. Russel and J. Simons, Proc. Roy. Soc., A217 (1953) 271.

74. D. Britton,/

74.	D. Britton, N. Davidson, W. Gehman and G. Schott,	J. Chem. Phys., 25 (1956) 804.
75.	D. Bunker and N. Davidson,	J. Amer. Chem. Soc., 80 (1958) 5085
76.	R.L. Strong, J.C.W. Chien, P.E. Graf and J.E. Willard	J. Chem. Phys., 26 (1957) 1287
77.	M.I. Christie,	J. Amer. Chem. Soc., 84 (1962) 4066
78.	G. Porter and J.A. Smith,	Proc. Roy. Soc., A261 (1961) 28
79.	G. Porter and J.A. Smith,	Nature, 184 (1959) 446.
80.	G. Porter,	Dis. Faraday Soc., 33, 34 (1962) 198
81.	E.T. Butler and M. Polanyi,	Nature, 146 (1940) 129.
82.	J.L. Jones,	J. Amer. Chem. Soc., 60 (1938) 1877
83.	R.A. Ogg,	J. Amer. Chem. Soc., 56 (1934) 526
84.	R.A. Ogg,	J. Amer. Chem. Soc., 56 (1934) 532
85.	E.W.R. Steacie,	Atomic and Free Radical Reactions, Reinhold, 1954 page 397
86.	S.W. Benson,	J. Chem. Phys., 38 (1963) 1945
87.	S.W. Benson and A.N. Bose,	J. Chem. Phys., 37 (1962) 2935
88.	J. Glass and C.N. Hinshelwood,	J. Chem. Soc., (1929) 1817
89.	J.L. Jones and R.A. Ogg,	J. Amer. Chem. Soc., 59 (1937) 1939
90.	J.L.Holmes and A. Maccoll,	J. Chem. Soc., (1963) 5919
91.	S.W. Benson and H. Teranishi,	J. Chem. Phys., 40 (1964) 2946
92.	R.A. Ogg and M. Polanyi,	Trans. Faraday Soc., 31 (1935) 482
93.	R.A. Ogg,	J. Amer. Chem. Soc., 56 (1934) 526
94.	J.H. Sullivan,	J. Phys. Chem., 65 (1961) 722
95.	S.W. Benson and R. O'Neal,	J. Chem. Phys., 34 (1961) 541
96.	M.C. Flowers and S.W. Benson,	J. Chem. Phys., 38 (1963) 882
97.	S.W. Benson and D.B. Hartley,	J. Chem. Phys., 39 (1963) 132
98.	S.W. Benson and P.S. Nangia,	J. Chem. Phys., 41 (1964) 530
99.	S.W. Benson and A. Bose,	J. Chem. Phys., 39 (1963) 132
100.	J.A. Guercione/	

100. J.A. Guercione and M.H.J. Wijnen, J. Chem. Phys., 38 (1963) 1

101. J.H. Knox, Gas Chromatography, Methven, 1962, page 91.

102. D.H. Desty, Gas Chromatography, Butterworth, 1960.

103. Reference 101, page

104. J.C. Sternberg, W.S. Gallaway, D.T.L. Jones, Gas Chromatography, Academic Press Inc., 1962.

105. A.G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules, 2nd Ed.

106. G. Hertzberg, Molecular Spectra and Molecular Structure, Spectra of Diatomic Molecules, 2nd Ed., D. Van Nostrand, 1953.

107. T.L. Cottrell, Strengths of Chemical Bonds, Butterworth, 2nd Ed., 1958

108. D.P. Stevenson, Trans. Faraday Soc., 49 (1953) 867

109. G.C. Fettis and A.F. Trotman-Dickenson, J. Amer. Chem. Soc., 81 (1959) 5260

110. D.P. Stevenson, Disc. Faraday Soc., 10 (1951) 35

111. S.J. Ashcroft, A.S. Carson, W. Carter and P.G. Lange Trans. Faraday Soc., 506 (1965) 225

112. S.W. Benson, Foundation of Chemical Kinetics, McGraw Hill 1960.

113. M.G. Evans and M. Polanyi, Trans. Faraday Soc., 34 (1938) 22

114. A.F. Trotman-Dickenson, Gas Kinetics, Butterworth, 1952, page 231.

115. E.T. Butler and M. Polanyi, Trans. Faraday Soc., 39 (1943) 19

116. G.C. Fettis and A.F. Trotman-Dickenson, J. Chem. Soc. (1961) 3037

117. Selected Values of Chemical Thermodynamic Properties, Circular 500, National Bureau of Standards, U.S.A.

118. G.B. Kistiakowsky and van Artsdalen, J. Chem. Phys., 12 (1944) 469

119. G.S. Rushbrooke, Introduction to Statistical Thermodynamics, Oxford, 1949.

120. L. Pauling/